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RANEY TYPE COPPER CATALYST
IN
CATALYTIC HYDROGENATION

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ABSTRACT

A kinetic study of the catalytic hydrogenation of compounds with Raney copper was made to determine how effective such a catalyst would be in reducing various groups. An investigation of this nature had not been undertaken with Raney copper previously.

With the pressure of hydrogen maintained throughout at 1000 ± 50 psi., a high pressure micro reaction vessel equipped with a shaking mechanism and heating jacket was employed. Glass liners were invariably used to prevent contamination of the reaction mixtures. The total volume of the system, including the liner, was approximately 38 ml.

The rates of hydrogenation were first order with respect to hydrogen pressure and zero order with respect to hydrogen acceptor. The rate was directly proportional to the catalyst weight, when the catalyst weight remained below a certain limit. This limiting weight of catalyst varied with different catalysts because some would pack tighter than others and large amounts of these were not shaken from the bottom of the liner during reaction. The result was that equilibrium between catalyst and hydrogen acceptor was not attained and, therefore, the rate was smaller than for smaller amounts of catalyst. Consequently, the amount of catalyst was kept below one g. in all other phases of this work.

Raney copper catalysts were prepared from several different alloys made from the metals in this laboratory, containing various amounts of copper and aluminum. The preparation of a Raney metal catalyst consists of digestion of the aluminum alloy of the metal with sodium hydroxide, whereupon the aluminum is dissolved from the surface leaving this surface active for hydrogenation catalysis. The largest rate for the hydrogenation of acetone was obtained from a catalyst which originally contained the highest percentage (60 per cent) aluminum.

By varying the procedure for preparing the catalyst, it was found that the temperature was important. At lower temperatures of addition of alloy to sodium hydroxide solution and of digestion of the slurry after the addition was completed, a more active catalyst resulted. It was possible, by adding the copper-aluminum alloy to the sodium hydroxide at temperatures between 0 and 10° C., and digesting the slurry for 45 minutes at 20° C., to get a catalyst of maximum activity. The rate of hydrogenation of acetone with this catalyst was approximately 70 per cent of the rate with Raney nickel.

The process of aging decreases the rate of hydrogenation with these copper catalysts just as it does with many other catalysts including Raney nickel. The loss of activity of copper was approximately linear with time over a period of one year. These catalysts lost one-third of their activity,

as measured by the rate of hydrogenation of acetone, in five months. For comparison, Raney nickel loses one-third its activity in approximately 1.5 months.

An interesting prospect for further study of these catalysts would be a determination of whether the catalyst is poisoned by materials, such as sulfur containing compounds, which very readily retard hydrogenations with Raney nickel. Since the rate of reaction is smaller after aging, all rate constants determined in this work were corrected for this.

Besides acetone, other carbonyl compounds, benzaldehyde and propionaldehyde were found to be readily reduced by Raney copper to the corresponding alcohols. The apparent activation energies for these compounds decreased in the order: propionaldehyde, acetone, and benzaldehyde. A further study might be made of a series of aliphatic and aromatic carbonyl compounds to determine if the energy of activation is the same for closely related compounds. It was determined in this work that the activation energies differed for the different catalysts with the same hydrogen acceptor.

Nitro groups, such as are found in nitrobenzene and 1-nitropropane, reduced less readily than similar compounds which contain carbonyl groups. The first order rate constant for the hydrogenation of 1-nitropropane was 16.5 $min.^{-1}$ $g.^{-1}$ at 127°C. for a catalyst which reduced acetone at a rate of 87.1 $min.^{-1}$ $g.^{-1}$ at the same temperature.

Unsaturated compounds are also less readily hydrogenated than carbonyl compounds, except where the double bonds are conjugated with other groups. Thus, 2-pentene reduced at a rate of 10.10 $min.^{-1}$ $g.^{-1}$ with a catalyst which reduced acetone at a rate of 75.33 $min.^{-1}$ $g.^{-1}$. On the other hand, the same catalyst reduced the double bond of mesityl oxide, where the double bond is conjugated with a carbonyl group, at a rate of 62.89 $min.^{-1}$ $g.^{-1}$. In general, straight chain unsaturated compounds reduce faster than unsaturated ring compounds. Benzene is not reduced upon treatment with hydrogen and Raney copper catalyst.

The hydrogenation of d-limonene was followed through the use of a polarimeter. The change in optical activity as the reaction progressed showed that the exo double bond was reduced first. The optical activity decreased slightly until 50 per cent reaction, after which it dropped linearly until complete reduction. d-Carvomenthene, the initial product is optically active, whereas the final product, p-menthane, is inactive. The rate of reduction of the endo bond was determined by calculating the rate of the half-hydrogenated product of d-limonene. The rate of the exo bond was approximately twice the rate of the endo bond.

Mesityl oxide reacted in a step-wise manner also, giving as an initial product 4-methyl-2-pentanone. The rate of reduction of the double bond was about four times that of the carbonyl group.

A further study could be made on compounds where the carbonyl group and double bond, for instance, are not conjugated. It is logical to assume that the carbonyl group would be preferentially reduced in a case such as this. Raney nickel generally reduces nitro groups and double bonds preferentially.

Another possible investigation could be made on the activity of Raney copper catalysts in dehydrogenation. For instance, in the dehydrogenation of alcohols with Raney nickel, some of the product consists of hydrocarbon produced by hydrogenolysis of the alcohol. Through such a study it could be determined whether copper would do this. It is thought that it would not remove the oxygen. Its relatively high rate of hydrogenation of carbonyl compounds suggests that it may be a good dehydrogenating catalyst also. Raney copper catalysts could be compared with other forms of copper concerning their relative rates of dehydrogenation. Such a study has not been made previously.

Throughout this work, it was found that the presence of both organic and inorganic acids either slowed or stopped the reaction. Impure benzaldehyde, containing benzoic acid, hydrogenated at one-sixth the rate of the freshly distilled material. 2-Pentene prepared by dehydration of 3-pentanol with sulfuric acid was unreacted upon until treated overnight with sodium hydroxide. Cinnamic acid did not react to an appreciable extent unless the sodium salt was made from it.

The addition of sodium hydroxide to the reaction mixture increased the rate of hydrogenation of cyclohexene also, but had no exhilarating effect with nitrobenzene or acetone. The black color of the original catalysts changed to red after reactions in which any acid was present.

Besides Raney copper, other catalysts were made from several different alloys. Copper was added to nickel in increasing percentages by weight, while the aluminum percentage remained at 50 per cent. The rate of hydrogenation of acetone decreased from 100 per cent nickel to 50 per cent of both nickel and copper. As the copper percentage was increased further, the rate again increased. It would be interesting to determine the surface areas of these catalysts, comparing them with the rates.

The inclusion of 0.6 per cent cadmium in the copper exerted a poisoning effect. The resulting catalyst had a rate only one-third that of the pure copper. Finally, replacement of aluminum by zinc resulted in a less active catalyst since zinc is less readily dissolved by base.

CHAPTER I

INTRODUCTION

Since 1927, when Raney[1] first introduced the use of a nickel catalyst prepared by treating an aluminum-nickel alloy with sodium hydroxide, Raney catalysts have found a wide range of applicability in both industrial and laboratory hydrogenations. Among the Raney metal catalysts that have been studied besides nickel are cobalt and copper.

The first work done on a Raney type copper catalyst was reported by Faucounau[2], who treated copper alloys with sodium hydroxide solution. Faucounau studied a catalyst prepared from a copper-aluminum-zinc alloy (Cu 45 per cent, Al 50 per cent) known as Devarda's alloy and a catalyst prepared from an aluminum bronze (about 10 per cent aluminum). The latter catalyst was ineffective, but the former hydrogenated aldehydes at 125-150°, ketones at 90-100°, and limonene at 200°. Phenylacetylene exploded at 80°, after which the temperature of the reaction vessel rose to 175°. He stated that cyclohexene, α-pinene, and benzene would not hydrogenate.

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[1] M. Raney, U. S. Patent 1,628,190 (May, 1927).

[2] L. Faucounau, Compt. rend., 203, 406 (1936); Bull. soc. chem., (5), 4, 58, 63 (1937).

Hachihama[3] and co-workers found that Raney copper catalysts hydrogenated furfural to furfuryl alcohol. When one per cent nickel was incorporated in the alloy from which the catalyst was made, the products were methyl furan and straight chain alcohols.

Mizuguchi and Iwase[4] also studied the hydrogenation of furfural with Raney copper catalyst as well as with reduced copper catalyst and Adkins' copper chromite catalyst[5]. They found Adkins' catalyst superior in this hydrogenation.

In a similar study with benzene and naphthalene[6], using the same catalysts, Mizuguchi and Yagi found reduced copper catalyst had the best catalytic activity, but the least durability.

Van Mechelen and Jungers[7] made a comparative study of the hydrogenation of aliphatic ketones on Raney nickel and Raney copper catalysts. These workers also used Devarda's alloy for preparing the Raney copper catalysts, varying the temperature and length of digestion with sodium hydroxide.

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[3]Y. Hachihama, K. Kawata, and M. Imoto, J. Soc. Chem. Ind. Japan, 45, 297 (1942).

[4]J. Mizuguchi and M. Iwase, J. Soc. Chem. Ind. Japan, 46, 1037 (1943).

[5]H. Adkins, Reactions of Hydrogen (Madison, Wisconsin: University of Wisconsin Press, 1937).

[6]J. Mizuguchi and Y. Yagi, J. Chem. Soc. Japan, 65, 691 (1944).

[7]C. C. van Mechelen and J. C. Jungers, Bull. soc. chim. Belges, 59, 597 (1950).

They found these approximate results:

(1) The activation energy for the hydrogenation of acetone varied for different catalyst preparations from 8.5 to 11.9 kilocalories per mole.

(2) The most active catalyst they obtained resulted from a digestion of the alloy with 250 g. of sodium hydroxide per liter at 60° for five hours.

(3) At a higher temperature, 90-100°, and for shorter digestion periods, three hours, the catalysts were less active.

The rates of hydrogenation listed in the work of van Mechelen and Jungers were expressed in moles of product per minute per gram of catalyst; however, since they did not mention the volume of the apparatus, these rates cannot be compared with those found in this work.

The necessity for including such data as the volume of the hydrogenation equipment was shown by Smith and co-workers[8], who had earlier reported the first systematic kinetic study of the catalytic hydrogenation of liquid hydrogen acceptors[9].

It seemed desirable, therefore, to investigate systematically various Raney copper catalysts and their ability to hydrogenate different organic compounds. A number of alloys were used to prepare catalysts under different sets of conditions

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[8] H. A. Smith and J. F. Fuzek, J. Am. Chem. Soc., 70, 3743 (1948).

[9] H. A. Smith, D. M. Alderman, Jr., and F. W. Nadig, ibid., 67, 272 (1945).

in order to determine the alloy and the preparation which resulted in the most active catalyst.

An important facet of the study of catalysts is the loss in activity brought about by aging of the catalyst. Smith, Bedoit, and Fuzek[10] made a study of aging of catalysts and its effect on the rate of hydrogenation of d-limonene with Raney nickel. They found that the rate decreased markedly with aging. A similar study of aging of Raney copper catalysts was investigated here.

Other factors studied in this work include the effect on the rate constant of sodium hydroxide added to the hydrogenation mixture, as well as effects produced by adding other metals to copper-aluminum alloys.

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[10]H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, ibid., 71, 3769 (1949).

CHAPTER II

BASIC KINETIC LAWS OF CATALYTIC HYDROGENATION

Rates of Surface Reactions.--One of the most fundamental methods of expressing the rate of any reaction, including a surface reaction, is to treat it as moles or molecules of reactant disappearing per second. The rate of disappearance of a reactant is -dn/dt moles per second if n is the number of moles of a reactant present at time t. If the number of moles of a product present at time t is n', the rate of appearance of that product is, then, dn'/dt.

It must be remembered that there may be a numerical difference in the rate according to whether reactant or product is considered. For example, if the stoichiometric equation for a reaction is

$$A + 2B = 3C, \qquad (1)$$

the rate of disappearance of B is twice that of A, while the rate of appearance of C is three times the rate of disappearance of A.

Instead of expressing the rate in terms of the number of moles of reactant or product per unit time it may be expressed as the rate of decrease of concentration of a reactant or as the rate of increase of concentration of a product. For

a reactant at a concentration c at time t, the rate of disappearance is -dc/dt and for a product at concentration c' at time t, the rate of appearance is dc'/dt.

If the reactants and product are gaseous, then concentrations, and also rates of reaction, may be expressed in terms of pressures. This is likewise true for a hydrogenation of a compound in the liquid phase, where the solubility of hydrogen in the liquid is proportional to the gas pressure. The rates of disappearance and appearance, respectively, for a reactant of pressure p at time t and for a product of pressure p' at time t are -dp/dt and dp'/dt.

The rates expressed in these different ways are all related. For ideal gases, pressures are related to concentrations by the equation

$$p = cRT, \tag{2}$$

where c is the concentration in moles per unit volume, R is the gas constant, and T is the absolute temperature. Thus, at constant temperature, dp/dt is related to dc/dt by the constant factor RT. In most fundamental kinetic studies, the temperature of the system is maintained constant and in this work the same holds true.

By the equation

$$p = n/V, \tag{3}$$

where V is the volume of the system, it follows that at constant volume, dc/dt is related to dn/dt by the constant factor

1/V. If the volume is not constant the rate in concentration units, -dc/dt, is equal to -d(n/V)/dt, which is not related to -dn/dt by any simple factor. The use of a constant volume in this study precludes the necessity of dealing with volume changes at any greater length.

Order of Surface Reactions.--If the rate of any reaction varies with the concentrations of the reactants in a particularly simple manner, the kinetics are specified by stating the order of the reaction. A reaction whose rate depends solely on the first power of the concentration of one reactant, or pressure of one reactant in the case of gaseous reactants, is said to be of the first order with respect to that reactant. When the rate is proportional to the product of two reactant concentrations, it is of the first order with respect to each of the reactants, but the rate of the over-all reaction is of the second order.

If the rate is related to the reactant concentrations C_A, C_B, et cetera, by an equation of the form

$$-dc/dt = kC_A^{\alpha} C_B^{\beta} \ldots, \qquad (4)$$

where $\alpha, \beta, \ldots$, are constants, the reaction is said to be of the α-th order with respect to A, the β-th with respect to B. et cetera. The over-all reaction order, n, is

$$n = \alpha + \beta + \ldots. \qquad (5)$$

Rate Constant for a Surface Reaction.--The term "rate constant",

also known as the "rate coefficient" and as the "specific reaction rate", is applied to the constant k in equation (4). The rate constant is numerically equal to the reaction rate when the reactants are present at unit concentrations.

The units of the rate constants depend upon those used for the concentration or pressure; for example, if moles per liter are used, the constant has the units (moles per liter)/(sec.)(moles per liter)^{n} where n, equal to $\alpha + \beta + \ldots$, is the over-all order; this reduces to mole^{1-n} liter^{n-1} sec.$^{-1}$.

Analysis of Experimental Data.--The most common method used in analyzing experimental kinetic data to determine the order of reaction and the rate constant is that of integration. According to this, the amounts of reactant or product at various times are fitted to integrated forms of the rate equations.

For instance, if the order of the reaction is zero, and if the concentration of the reactant expressed in pressure is p at time t, the differential form of the rate equation is

$$-dp/dt = k(p)^{0} = k. \qquad (6)$$

Upon integration, this becomes

$$-p = kt + \text{constant}. \qquad (7)$$

A plot of the pressure at various times would yield a straight line, the slope of which would be -k. The units of k, when p is in atmospheres, is atm. sec.$^{-1}$.

If the reaction is of the first order, the differential

form of the rate equation is

$$-dp/dt = kp, \tag{8}$$

which means that the rate of disappearance of reactant is proportional to its pressure at any particular instant.

Integration of this equation gives

$$-\ln p = kt + \text{constant} \tag{9}$$

or

$$-\log p = kt/2.303 + \text{constant} \tag{10}$$

Thus, if log p is plotted against t, a straight line is obtained. The slope is equal to k/2.303, and the rate constant may be obtained by multiplying this slope by 2.303. If equation (9) is integrated between the limits of pressure p_1 at time t_1 and pressure p_2 at time t_2, the equation is

$$-\ln p_2 - (-\ln p_1) = k(t_2 - t_1). \tag{11}$$

Converting to common logarithms and rearranging, one obtains

$$\log \frac{p_1}{p_2} = \frac{k(t_2 - t_1)}{2.303}. \tag{12}$$

If p_1 is replaced by p_o (the pressure at $t_1 = 0$), and p_2 by p (the pressure at any time t), the equation becomes

$$\log \frac{p_o}{p} = \frac{kt}{2.303}. \tag{13}$$

The units of the rate constant k are in reciprocal seconds if t is in seconds.

Since we are dealing with the hydrogenation of hydrogen acceptors in the liquid phase, in equation (13) the fugacity of hydrogen is assumed to be proportional to the mole fraction of the hydrogen dissolved in the liquid phase. At the pressures used in this work the fugacities do not equal the hydrogen pressures and equation (13) is more exactly written

$$\log \frac{p_o \gamma_o}{p \gamma} = \frac{kt}{2.303} \qquad (14)$$

where γ is the activity coefficient of the hydrogen gas. If the ratio po/p is not large, $\gamma o/\gamma$ becomes unity and equation (14) reduces to equation (13), which may be used to express the rate within experimental error.

The Dependence of the Rate on Amount of Catalyst and Gas Volume. The rate of a surface reaction, and thus also the rate constant, is dependent on the area of the catalyst surface for any specific batch of catalyst and on the total gas volume. It is usually the case that the number of molecules reacting per unit time is directly proportional to the weight of any given catalyst. If the amount of a specific catalyst preparation, and thus the surface area, is increased tenfold, the number of molecules reacting per unit time is increased tenfold and for constant volume the rate is also increased tenfold.

Thus, in this work, the observed rate constant is divided by the weight of the catalyst used. It must be remembered in connection with surface area that a variation in rate may occur when two catalysts prepared in the same manner have different surface areas per unit weight.

If the total volume of the reaction system is increased, the molecules transformed are distributed over the larger volume, and the rate is reduced in inverse proportion to the volume[1]. The rate equation may then be written

$$-\frac{dp}{dt} = \frac{ks}{V} p_A^{\alpha} p_B^{\beta} \ldots \qquad (15)$$

where V is the total volume and s is the surface area which is proportional to the amount of a specific catalyst present.

Since the same apparatus was used in all cases in this work, the volume was the same throughout. If the rate constant values are to be compared with values of other workers, they must be multiplied by the volume of the system which was 37.8 $\pm$ 3.0 ml.

Temperature Dependence of the Rate Constant.--The temperature dependence on the rate of reaction and thus on the rate constant is important in studies of catalyst activity. According to the Arrhenius law, the rate constant k varies with the

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[1]H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, J. Am. Chem. Soc., 71, 3769 (1949).

temperature in the following way:

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2} . \qquad (16)$$

Here E is the energy of activation of the reaction, R is the gas constant, and T is the absolute temperature. The activation energy was interpreted by Arrhenius as the energy that the reactant molecules had to acquire in order to react. This law is strictly applicable to elementary single stage processes only, such as an adsorption process or a reaction of an adsorbed substance. When we are dealing with an over-all surface reaction, which involves both adsorption and reaction, it is not necessarily applicable. An analysis of this equation will follow in the next chapter.

When equation (16) is integrated between the limits of k_1, the rate constant at temperature T_1, and k_2, the rate constant at T_2, it becomes

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303\ RT} \frac{1}{T_2} - \frac{1}{T_1} . \qquad (17)$$

Thus, the plot of log k versus 1/T gives a straight line, the slope of which is equal to $-E_a/2.303R$, where E_a is the "apparent energy of activation". By multiplying the slope of the line by 2.303R, a value is obtained for E_a.

The purpose of finding the apparent energy of activation is to be able to predict the reaction rate at other temperatures and thus be able to compare the activities of different catalysts at the same temperature, through the rates of reaction.

CHAPTER III

THEORY OF HETEROGENEOUS CATALYSIS

Adsorption.--The previous chapter dealt with the purely experimental aspects of surface reactions. Consideration will now be given to the various theories of catalysts action.

The only successful explanation of surface catalysis has been in terms of the theory that adsorption of reactant molecules must occur, and that the reaction occurs in the adsorbed films. Such a view was first proposed by Faraday in 1825. It was for a time thought that the main effect of the catalyst was to concentrate the reactant molecules and thus increase their chance of reaction. This is not true, since in certain cases different surfaces give rise to different products from the same reactants, which indicates that specific forces are involved.

The conclusion has been reached that there are two main types of adsorption which are clearly distinguishable: van der Waals adsorption and chemisorption. In van der Waals or physical adsorption, the molecules are held to the surface by physical forces which correspond in magnitude to those involved in the van der Waals equation of state for gases. The heat evolved during such an adsorption is about the same as is evolved during the liquifaction of the gas, i.e., a few hundred calories per mole. The chemical activity of the adsorbed

material is not markedly altered by this type of adsorption. Van der Waals adsorption would not, therefore, be important with stable molecules, although it does play a part in reactions of atoms and free radicals at surfaces.

Chemisorption, on the other hand, occurs when the molecules are held to the surface by valence forces. The heats evolved are of the same order as those involved in chemical reactions.

One of the special features of chemisorption is that after a surface has become covered with a single layer of adsorbed molecules, it is essentially saturated so that additional chemisorption cannot take place[1,2]. Another feature is that the process of chemisorption may often have an appreciable activation energy, and hence may sometimes be a slow process[3,4]. The third special feature of chemisorption is that there is frequently a considerable variation in the adsorptive capacities of the various surface sites[5,6,7]. Varying degrees of unsaturation occur even on the most polished surfaces which are, in

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[1]I. Langmuir, J. Am. Chem. Soc., 38, 221 (1916); ibid., 40, 1361 (1918).

[2]J. K. Roberts, Proc. Roy. Soc., A 152, 445 (1935).

[3]H. S. Taylor, J. Am. Chem. Soc., 53, 578 (1931); Chem. Rev., 9, 1 (1931).

[4]K. J. Laidler, Catalysis, Vol. I (New York: Reinhold Publishing Co., 1954) p. 77.

[5]H. S. Taylor, Proc. Roy. Soc., A 108, 105 (1925); J. Phys. Chem., 30, 145 (1926).

[6]F. F. Valkenshtein, Zhur. Fiz. Khim., 23, 917 (1949).

[7]R. N. Pease and R. Stewart, J. Am. Chem. Soc., 47, 1235 (1925).

reality, not perfectly smooth. These points of unsaturation where the molecules may be adsorbed are not occupying fixed positions on the surface, but are constantly being created and destroyed with the movement of excited electrons in the lattice.

Diffusion Theory of Surface Catalysis.--A necessary part of a reaction on a surface is the diffusion to the surface of the reactant molecules and the diffusion away from the surface of the product. On a nonporous surface, in order for diffusion to be the slow step, it is necessary for the diffusion layer to be very thick and, in fact, to be a visible layer. This is not generally encountered in nonporous catalysts. A rate controlling slow step of diffusion is not to be expected in liquid phase hydrogenations if the apparatus is shaken during the reaction.

Langmuir Mechanisms.--Since adsorption and desorption processes both involve appreciable energies of activation, either one may be the slow or rate controlling step in surface catalysis. The actual chemical transformation could also be the slow step.

Langmuir[8] considered a number of mechanisms for catalysis, one of which was later applied by Hinshelwood[9]. According

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[8] I. Langmuir, Trans. Faraday Soc., 17, 621 (1921).

[9] C. N. Hinshelwood, Kinetics of Chemical Change (New York: Oxford University Press, 1926) p. 145.

to this mechanism, the reactant or reactants are considered to be in adsorptive equilibrium with the surface, reaction involving the adsorbed molecules. The quantitative treatment of reactions occuring by this mechanism involves obtaining an expression from use of the adsorption isotherms for the concentrations of reactant molecules on the surface, and then expressing the rate of reaction in terms of these surface concentrations. The rate of reaction can then be expressed in terms of the concentrations of gaseous reactants.

If there is a single reactant, the process on the surface is probably unimolecular. In a reaction of this type where the adsorption equilibrium can be regarded as undisturbed by the occurrence of the reaction and where the rate is proportional to the concentration of the material on the catalyst, we may write that

$$v = k\,\theta, \tag{18}$$

where v is the rate of the reaction, k is the rate constant, and θ is the fraction of catalyst surface covered by the material. θ is called the Langmuir isotherm and will be derived in the next section.

On the other hand, if there are two reactants, A and B, these must be adsorbed on neighboring surface sites for reaction to occur, and the probability that this occurs is proportional to the individual concentrations of adsorbed A and adsorbed B. Thus

$$v = k\theta\theta', \tag{19}$$

where θ and θ' are the fractions of surface covered by reactants A and B, respectively.

The other mechanism which Langmuir considered might be applicable to reactions between two species, A and B, is now known as the Rideal mechanism. According to this mechanism, only one reacting substance has to be adsorbed, and the reaction occurs between a gas molecule and an adsorbed molecule. Rideal suggested that this mechanism may apply to certain reactions involving hydrogen such as the hydrogenation of ethylene.[10] However, more recent work by Laidler indicates that this is probably not the case[11].

Langmuir Adsorption Isotherms.--The Langmuir isotherm applies to a perfectly smooth surface where there are no interactions between adsorbed molecules. Adsorption which obeys the Langmuir isotherm may be termed ideal adsorption.

To derive the isotherm for a unimolecular reaction, we shall consider a gas at pressure p in equilibrium with a surface. The fraction of the catalyst surface which is covered by adsorbed gas is denoted by θ, so that $1 - \theta$ is the fraction of surface bare. The rate of adsorption v_1, then, is proportional to the gas pressure and to the fraction of surface uncovered since adsorption can only occur when a gas molecule

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[10] E. K. Rideal, Proc. Cambridge Phil. Soc., 35, 130 (1949); Chemistry and Industry, 62, 335 (1943).

[11] K. J. Laidler, J. Phys. Colloid Chem., 55, 1067 (1951).

strikes a bare part of the surface.

The rate may be written as

$$v_1 = k_1 p\ (1 - \theta) \tag{20}$$

where k_1 is a constant. The rate of desorption v_{-1} depends on the amount of gas adsorbed, and is therefore proportional to θ:

$$v_{-1} = k_{-1}\theta. \tag{21}$$

At equilibrium the rates of adsorption and desorption are equal and

$$k_1 p\ (1 - \theta) = k_{-1}\theta \tag{22}$$

or,

$$\frac{\theta}{1 - \theta} = \frac{k_1}{k_{-1}}\ p \tag{23}$$

$$= Kp \tag{24}$$

where K, equal to k_1/k_{-1}, is an equilibrium constant for adsorption.

Rearrangement of this equation gives

$$\theta = \frac{Kp}{1 + Kp}\ , \tag{24}$$

θ being the fraction of surface covered.

The isotherm for two gases adsorbed on the same surface is important in connection with chemical reactions between two

substances. The fraction of surface covered by molecules of type A is θ, and the fraction covered by B is θ'. The rate of adsorption of A is given by

$$v_1 = k_1 p\ (1 - \theta - \theta'), \tag{25}$$

where p is the partial pressure of A, $1 - \theta - \theta'$ is the fraction of surface that is bare. The rate of desorption of A is given by

$$v_{-1} = k_{-1}\theta, \tag{26}$$

Equating these rates gives

$$\frac{\theta}{1 - \theta - \theta'} = Kp, \tag{27}$$

where K is equal to k_1/k_{-1}.

In a similar manner, it can be shown that for reactant B

$$\frac{\theta'}{1 - \theta - \theta'} = K'p', \tag{28}$$

where p' is the partial pressure of B and K' is equal to the ratio of the rate constants for the adsorption and desorption of B.

Solution of equations (27) and (28) gives

$$\theta = \frac{Kp}{1 + Kp + K'p'} \tag{29}$$

and

$$\theta' = \frac{K'p'}{1 + Kp + K'p'} \qquad (30)$$

for the fractions covered by A and B respectively.

Kinetics of Hydrogenation.--If the surface reaction of hydrogenation occurs by the Langmuir-Hinshelwood mechanism, the rate of the reaction between adsorbed A and adsorbed B is proportional to the probability that A and B molecules are adsorbed on neighboring sites. This in turn is proportional to the product of the fractions covered by A and B. Thus, the rate of reaction is $v = k\theta\theta'$. Substituting the isotherms (29) and (30) gives

$$v = \frac{kKK'pp'}{(1 + Kp + K'p')^2} \qquad (31)$$

If the reaction is the catalytic hydrogenation of a material in the liquid phase, it is probable that the amount of adsorbed substance is constant during most of the reaction. There is a concentrated layer of substance over the catalyst, which replaces a product molecule as soon as it is desorbed. Thus, when the fraction of surface covered by the acceptor is constant, the rate equation (31) becomes

$$v = \frac{k'Kp}{1 + Kp + K'p')}, \qquad (32)$$

where $k' = kK'p'$.

If the reactants are weakly adsorbed, the terms Kp and

K'p' are small and may be neglected in comparison to one so that the rate is

$$v = k'Kp \tag{33}$$

or,

$$-\frac{dp}{dt} = \underline{k''p}, \tag{34}$$

where $k'' = k'K$.

The integrated rate equation is

$$\log \frac{p_o}{p} = \frac{kt}{2.303}, \tag{35}$$

where p_o is the pressure of hydrogen at time $t = 0$, and p is the pressure at any time t thereafter.

If the Rideal mechanism applies and the reaction occurs between an adsorbed A molecule and an unadsorbed B molecule, it can be shown that the fraction of surface covered by A is given by

$$\theta = \frac{Kp}{1 + Kp + K'p'} \tag{36}$$

assuming that A and B molecules can both be adsorbed on the catalyst. The rate is now proportional to this fraction and the pressure p' of B so that

$$v = k\theta p', \tag{37}$$

or,

$$v = \frac{kKpp'}{1 + Kp + K'p'} . \qquad (38)$$

If B molecules are not adsorbed at all, the term K'p' in the denominator drops out, and the equation becomes

$$v = \frac{kKpp'}{1 + Kp} . \qquad (39)$$

Such data as is available suggests that of the two possibilities, equations (31) and (38), equation (31) is the more probable[12].

Balandin[13,14] discusses catalytic hydrogenations of gases at length and proposes that there are two types of active centers. He also assumes that adsorption equilibrium occurs before reaction can take place. He asserts that the standard equation for one kind of active center (equation 31) shows a maximum should occur, but since at high pressure the reaction becomes zero order, the rate he proposes[15] is

$$v = \frac{kKp}{1 + KP + K'p + K''p''} \cdot \frac{K_1'p'}{1 + K_1'p' + K_1p + K_1''p''} . \qquad (40)$$

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[12]K. J. Laidler, Catalysis, Vol. I (New York: Reinhold Publishing Co., 1954) p. 154.

[13]A. A. Balandin, J. Gen. Chem. (U.S.S.R.) 15, 608 (1945).

[14]A. A. Balandin, Bull. acad. sci. (U.S.S.R) 1945, 339.

[15]A. A. Balandin, Acta Physicochim. (U.R.S.S.) 22, 81, 101, 338 (1947).

K, K', and K" are the equilibrium constants for adsorption and desorption of hydrogen, hydrogen acceptor, and product, respectively, on the first type of center C. The pressures or concentrations of hydrogen, hydrogen acceptor, and product are p, p', and p", respectively. K_1, K'_1, and K''_1 are the equilibrium constants for adsorption and desorption of hydrogen, hydrogen acceptor, and product, respectively, on the second type of active center C_1.

If the hydrogen acceptor is a liquid and covers most of type C centers to the exclusion of any other material, the terms Kp and K"p" are negligible and the equation becomes

$$v = \frac{kKp}{K'p'} \cdot \frac{K'_1 p'}{1 + K'_1 p + K_1 p + K''_1 p''} \qquad (41)$$

and canceling,

$$v = \frac{kKK'_1}{K'} \cdot \frac{p}{1 + K'_1 p + K_1 p + K''_1 p''} . \qquad (42)$$

Balandin assumes that K' = K", which indicates that the reactant and product are similarly oriented on the catalyst, and that p' + p" = 1. At high pressures, unity in the denominator can be neglected, and

$$v = \frac{kKK'_1}{K'} \cdot \frac{p}{K'_1 + K_1 p} . \qquad (43)$$

The rate is constant until p' becomes small and the rate falls since other terms become significant besides K'p'.

At low temperatures, the adsorption of hydrogen increases, $K_1 \gg K_1'$, and the reaction is zero order:

$$v = \frac{kKK_1'}{K'K_1} . \qquad (44)$$

This is in agreement with experiments on the hydrogenation of toluene in the gas phase with Raney nickel at temperatures below 190° C[16].

At high temperatures, because of the evaporation of hydrogen from the active centers, $K_1' \gg K_1$, and

$$v = \frac{kK}{K'} p. \qquad (45)$$

The rate is first order with respect to hydrogen as has been found experimentally with toluene at 190° C. and above[16].

Another mechanism which has been proposed for the hydrogenation of acetone and benzene in the gaseous phase leads to the equation

$$v = k \frac{K'p'}{1 + K'p'} \cdot \frac{Kp}{1 + Kp} . \qquad (46)$$

This theory, proposed by Herbo[17], calls for the adsorption of hydrogen acceptor on one type of center exclusively, and the

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[16] A. V. Lozovoi and M. K. Dyakova, J. Gen. Chem. (Russ.) 7, 2969 (1937); ibid., 8, 105 (1938); ibid., 9, 896 (1939); ibid., 10, 1 (1940).

[17] Cl. Herbo, J. chim. phys., 47, 454 (1950).

adsorption of hydrogen on another type, exclusively.

Herbo found at temperatures below 200° C. the rate was zero order and decided that the catalyst is covered simultaneously by both hydrogen and acetone, and $Kp \gg 1$ and $K'p' \gg 1$. At temperatures above 200° C. with the same pressure he found that the rate was proportional to the partial pressure of both acceptor and hydrogen. He assumed that the adsorption was negligible because of the evaporation of the materials from the catalyst, and $Kp \ll 1$ and $K'p' \ll 1$. The total pressure of the system was 760 mm during Herbo's investigations.

This theory is similar but simpler than Balandin's, which can be used in interpreting both liquid and gas systems. It appears that Balandin's theory is the best put forth so far, since it overcomes the objections to the Rideal mechanism and to the simple one-type site Langmuir-Hinshelwood mechanism.

Evidence for the fact that there are sites of varying activity on a reduced cupric oxide catalyst was presented by Russell and Ghering[18]. Oxygen poisoning experiments revealed that the heats of oxygen adsorption diminished as adsorption increased. Indirect oxygen poisoning, that is, removal of different amounts of oxygen by reduction of the poisoned catalyst, released a surface having portions of widely different hydrogenating capacities. These experiments also revealed

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[18] W. W. Russell and L. G. Ghering, J. Am. Chem. Soc., 57, 2544 (1935).

that a large fraction of the surface was catalytically active.

Other evidence for catalytic sites of varying activity was presented by Eley[19] in experiments with ethylene and hydrogen on a copper catalyst. This work showed that if ethylene is allowed to adsorb on a catalyst before hydrogen is introduced, the reaction is slow to start. This is attributed to the adsorption of ethylene on almost all of the available surface sites of any activity, and the necessity of hydrogen being adsorbed on a certain type of site before it can react. Thus, when hydrogen finally displaces some of the ethylene, the reaction begins.

The last mechanism which is possible in the hydrogenation of liquid hydrogen acceptors is a result of the diffusion of hydrogen through the liquid phase. If this process were slow enough, it could be the rate determining step. This appears unlikely, since the rate of diffusion of hydrogen through any given organic liquid should be the same whatever catalyst is used. Such is not, however, the case.

Whatever the mechanism is, it is important in comparing the activity of catalysts that the initial hydrogenation pressure be the same, so that the rates are determined at the same pressure on a rate versus pressure curve. Therefore, in this work the pressure of hydrogen has been maintained at 1000 psi., initially.

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[19]D. D. Eley, Advances in Catalysis, Vol I (New York: Academic Press, 1948) p. 157; Quart. Revs. 3, 209 (1949).

Activation Energies in Bimolecular Surface Reactions.--It has been shown in equation (31) that the rate law for a bimolecular reaction by a Langmuir-Hinshelwood mechanism takes the form

$$v = \frac{kKpK'p'}{(1 + Kp + K'p')^2} . \tag{47}$$

The Arrhenius law,

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2} , \tag{48}$$

applies to the rate constant k in equation (47), which is the rate constant for the reaction of the adsorbed reactant molecules. The temperature variation of the equilibrium constant K follows the analogous law

$$\frac{d(\ln K)}{dT} = - \frac{\lambda}{RT^2} \tag{49}$$

where λ is the heat evolved per mole of reactant gas A in the adsorption process. For reactant B, we have

$$\frac{d(\ln K')}{dT} = - \frac{\lambda'}{RT^2} \tag{50}$$

where λ' is the heat evolved per mole of gas B.

If the terms Kp and K'p' are small and thus can be neglected in equation (47), the rate is given by

$$v = kKpK'p'. \tag{51}$$

Then

$$\frac{d(\ln v)}{dT} = \frac{d(\ln kKK')}{dT} \tag{52}$$

$$= \frac{d(\ln k)}{dT} + \frac{d(\ln K)}{dT} + \frac{d(\ln K')}{dT}. \tag{53}$$

$$= \frac{E - \lambda - \lambda'}{RT^2}. \tag{54}$$

The apparent activation energy E_a is given by $E_a = E - \lambda - \lambda'$ and the apparent activation energy is the "true" activation energy E reduced by the heat of adsorption of the reactants.

The apparent activation energy will not be equal to the "true" activation energy no matter which of the mechanisms just discussed really holds. When comparing the activity of a single compound with various catalysts, it must be remembered that λ as well as λ' will change for different catalysts. Therefore, the only benefit derived from calculating the apparent energy of activation is to use it to find rates at other temperatures close to those that are known. Thus, it is possible to compare different catalysts whose rates have not been determined at exactly the same temperature by making use of the Arrhenius equation. Wherever necessary, this is what has been done in this work.

It is thought that the activation energies of adsorption of hydrogen and hydrogen acceptor are zero or close to zero[20,21,22]. If this is not so, these energies would also appear in the apparent activation energy.

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[20]H. S. Taylor, J. Am. Chem. Soc., 53, 578 (1931).

[21]O. Beeck, Rev. Mod. Phys., 17, 61 (1945).

[22]J. K. Roberts, Proc. Roy. Soc., A 152, 445 (1935).

CHAPTER IV

EXPERIMENTAL PROCEDURE

Materials

Hydrogen.--The hydrogen gas was supplied by the National Cylinder Gas Company, Atlanta, Georgia, and was used without further purification. The pressure of the full tank, approximately 2000 psi., was sufficient for this work where the initial pressures in each case were 1000 ± 50 psi.

Metals.--Aluminum in a granular form (8 mesh or finer) was obtained from the Matheson, Coleman, and Bell Company, East Rutherford, New Jersey. Copper metal shot and cadmium sticks were obtained from the Mallinckrodt Chemical Works, St. Louis, Missouri. Devarda's alloy, obtained from Mallinckrodt, was C. P. grade. C. P. grade nickel and zinc were obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey. The Raney-nickel alloy was obtained from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

Acetone.--Acetone was purified in two different ways. According to the first method[1], a solution of three g. of silver nitrate in 30 ml. of water and eight ml. of 10 per cent sodium

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[1] L. F. Fieser, Experiments in Organic Chemistry, Pt. II (New York: Heath and Co., 1941) p. 363.

hydroxide was added to 700 ml. acetone. The mixture was shaken for ten minutes, after which it was filtered, dried over calcium chloride for two days, and distilled. The acetone distilled at 55.4° C. at 746.9 mm. pressure, or at a corrected boiling point of 55.9° C. The column used for this fractionation was a five foot helix-packed column having approximately 40 theoretical plates. The material was collected at a reflux ratio of ten to one.

The second method of purification consisted in shaking 300 ml. of acetone with one g. of potassium permanganate and allowing the mixture to stand overnight. The resulting solution was filtered, dried overnight with calcium sulfate, then carefully distilled. The column used was a 20 inch tantalum-spiral packed column. The acetone, collected at a ten to one reflux ratio,had a corrected boiling point of 56.9° C.

2-Pentene.--2-Pentene was prepared from the hydrogenation of 200 ml. diethyl ketone with approximately three g. of Raney nickel catalyst. The reduction was run at 120° C. at an initial hydrogen pressure of 1500 psi. The product, 3-pentanol, was distilled (b.p. 115° C. corrected). Dehydration of 25 ml. of 3-pentanol was accomplished with three ml. of 75 per cent sulfuric acid. The final product, 2-pentene, boiled at 37.6° C. (corrected). This material was dried overnight with sodium hydroxide before use.

Liquid Hydrogen Acceptors.--Benzaldehyde, butyronitrile,

diethyl ketone, d-limonene, mesityl oxide, and propionaldehyde were obtained from the Eastman Kodak Company, Rochester, New York, and were white label grade. In Table 1, a list of the corrected boiling points obtained in this work, along with those reported in the literature[2], are given.

Allyl alcohol, 1-nitropropane, α-pinene, and styrene were practical grade materials obtained from the Eastman Kodak Company. The allyl alcohol was dried over calcium carbonate, then distilled without any other preliminary purification.

1-Nitropropane was purified by stirring in a warm dilute solution of sodium hydroxide, separating the organic material, washing with distilled water, and distilling[3]. It distilled at a temperature of 52° C. under a pressure of 159 mm.

α-Pinene was distilled in a nitrogen atmosphere and used without further purification.

Since the styrene was stabilized with t-butyl catechol, it was necessary to distill the hydrocarbon prior to use. It was observed that the rate constants were erratic unless the styrene was freshly distilled before each run. Consequently, this was done.

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[2]I. M. Heilbron, Dictionary of Organic Compounds (New York: Oxford University Press, 1943).

[3]O. Silberrad, British Patent 799 (Jan. 1912).

Table 1. Boiling Points of Liquid Hydrogen Acceptors

Compound	Boiling Point, °C. (corrected)	Boiling Point, °C. (literature)
Acetone	55.9, 56.9	56.2
Allyl alcohol	95.4-6.7	96-7
Benzaldehyde	176.9	179 /751 mm.
Benzene	80.5	80.1
Butyronitrile	117.2	117
Cyclohexene	82.8-3.3	84
1,3-Cyclohexadiene	80.8-2.8	83-4
Diethyl ketone	102.2	101.5
Ethyl alcohol	78.4	78.5
Ethyl oleate	204.7-7.7 /175 mm.	216-7 /151 mm.
n-Hexane	68.8	68.9
d-Limonene	177.1	178
Mesityl oxide	127.9	130-1
2-Methyl-2-butene	38.2-40.4	38.4
Nitrobenzene	130 /71 mm.	120.2 /50 mm.
1-Nitropropane	52 /159 mm.	130.5-1.5
α-Pinene	153.5	155-6
Propionaldehyde	48.1	47.5-9.0
Styrene	144.4	145.0-.8

A practical grade of ethyl oleate was distilled and used without further purification. It polymerized appreciably during the distillation, but further treatment was not given it.

Nitrobenzene was a technical grade obtained from the Will Corporation, and was purified by stirring in a warm dilute solution of sodium hydroxide. Separation of the organic layer, followed by a water wash and distillation under reduced pressure, gave a pure material.

Technical grade cyclohexene was distilled without further purification.

A 1,3-cyclohexadiene mixture containing about 20 per cent cyclohexene was obtained from Dr. Leon Zalkow. It was distilled before use.

Solid Hydrogen Acceptors.--A technical grade of trans-cinnamic acid was recrystallized three times from benzene.

Fumaric acid, likewise a technical grade, was recrystallized four times from carbon tetrachloride.

Maleic anhydride was purified by recrystallizing it four times from chloroform.

The corrected melting points for all of these appear in Table 2.

Solvents.--Among the solvents used in this work were C. P. grade n-hexane and spectro grade benzene.

Ethyl alcohol was distilled and used without further

purification.

The boiling points of these materials are listed in Table 1.

Apparatus

Reaction Vessel.--The high pressure reaction vessel used for the hydrogenations was the Aminco[4] micro apparatus equipped with heater, shaking mechanism, and reaction vessel with valve and gage. The required construction and operation of the superpressure equipment for hydrogenation has been discussed by Adkins[5].

The shaking mechanism consisted of a heavy cast iron base upon which was mounted a pedestal for supporting an oscillating trunnion. The heating jacket was attached to the trunnion, and the removable reaction vessel fitted inside the heater. A 1/8 horsepower motor was used to rock the vessel in an arc of about 30 degrees at 34 cycles per minute.

A manganese steel reaction vessel with an inside diameter of 3/4 inch and inside depth of six inches was used. The outside diameter was 2.57 inches and the outside length was 11.75 inches.

The compression closure consisted of four parts: (1) an outside cap which screwed on the reaction vessel;

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[4]American Instrument Company, Silver Springs, Maryland.

[5]H. J. Adkins, J. Am. Chem. Soc., 55, 4272 (1933).

Table 2. Melting Points of Solid Hydrogen Acceptors

Compound	Melting Point, °C. (corrected)	Melting Point, °C. (literature[6])
trans-Cinnamic acid	132.5	133
Fumaric acid	286-7	286-7
Maleic anhydride	54.0-.5	60, 53

[6] I. M. Heilbron, op. cit.

(2) thrust bolts; (3) a hardened steel ring which prevented the thrust bolts from marring the pressure head; and (4) the inner pressure head with a flat copper gasket.

The inner pressure head with the copper gasket fitted on the bomb, the inner head was connected to a needle valve, and the needle valve in turn attached to a dial pressure gage. The hardened steel ring was sealed on the inner head and the outside compression cap was screwed on the bomb. Since it is important that the amount of thrust bolt pressure applied on the periphery of the closure be uniform if no leakage is to occur, a torque wrench was used. The torque wrench was set at increasing amounts of force and the bolts tightened evenly until 35 foot pounds was attained.

Temperature Control.--The heating jacket had two interwoven elements wound in parallel and controlled with a three heat switch. With the switch in the "Low" position, both heater elements were in series to give quarter wattage. The heater was connected to a Powerstat voltage regulator, which in turn was connected to a constant voltage box. Thus, the temperature could be controlled accurately by varying the voltage supplied by the Powerstat. The temperature was measured by a calibrated Weston testing thermometer which fitted through the end of the heating jacket into a thermowell in the vessel.

Reaction Liners.--In order to prevent contamination of the reaction mixtures and corrosion of the bomb, it was necessary

to use glass liners. The liners used were made by the Consolidated Glass Works, Fordstown, Tennessee. They were fitted with ground glass tops and had an over-all length of six inches. A small hole was made in the side of the tube to admit hydrogen into the reaction mixture.

The volume of the bomb with liner was 33.1 ± 1 ml. The volume of the gage, calculated by absolute and pressure-drop methods[7], was 11.7 ± 2 ml. and the volume of hydrogen acceptor, catalyst, and alcohol was seven ml. The volume of the bomb when charged with catalyst, hydrogen acceptor, and liner therefore was 37.8 ± 3 ml.

Alloy Preparation.--The alloys were prepared from metals in a small electrical resistance furnace called the Handi-Melt Electric Furnace manufactured by the Jelrus Company, New York and supplied by the A. S. Lapine Company, Chicago, Illinois. The oven consisted of a metal base with a wooden handle upon which a heating element was attached. The temperature of the melt was measured by means of a thermocouple, and the maximum safe temperature for the apparatus was 1100° C. A carbon crucible fitting into the heating apparatus contained the metals to be alloyed. The equipment was provided with a clay cover to prevent oxidation of the metals. If the crucible was

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[7]E. F. Cox, "The Catalytic Hydrogenation of Quinolines at High Pressures", Master's Thesis, Georgia Institute of Technology, 1951.

more than three quarters full, it was noticed that the aluminum tended to oxidize, therefore the crucible was never more than half filled. The catalyst prepared from a melt which had oxidized was found to contain white particles of aluminum oxide which were insoluble in sodium hydroxide as ignited aluminum oxide is.

For alloys requiring a temperature greater than 1100°, a high frequency induction furnace made by the Lepel High Frequency Laboratories, New York, was used. High frequency currents generated heat only in the melting metals. The crucible used was of clay construction and was held in place by the copper coils through which the current passed. In order to keep the coils from becoming too hot, a current of cold water was passed through the center of the hollow tubes of which the coils were made.

While still molten, the alloys were well mixed with carbon stirring rods, then poured into a porcelain crock filled with cold water. This procedure usually left the pieces of alloy containing gas bubbles which facilitated their crushing.

Grinding of Alloys.--The alloys were pulverized in a Bantam Mikro-Pulverizer made by the Pulverizing Machinery Company, Summit, New Jersey. The Mikro-Pulverizer is an impact grinder consisting of a small hammer mill into which the alloy was introduced by means of a screw feed. The alloy is confined in a cylindrical area where the hammers are spinning.

The Mikro-Pulverizer is mounted on a cast iron base

with legs and casters. The main drive motor is 3/4 horsepower, making 3450 revolutions per minute. The electrical equipment is for use on a 110 volt, 60 cycle current. The pulverizer is equipped with a phosphor bronze mill housing and feed trough, stainless steel feed screw, chrome molybdenum rotor shaft, and bronze hopper. The hammers are drop forged steel tipped with abrasion resistant alloy.

When the particles of alloy become small enough, they are ejected from the hammer mill through a heavy stainless steel interchangeable screen and are collected in a bag placed beneath the screen. The screen used in this work was number 027 RD24G. This was the method used in reducing all the alloys to powders.

Digesting of Alloys.--For the digestion of the alloys, a 500 ml. round bottom flask was placed in a container of ice and water. The flask was equipped with a stirrer which was attached to an induction motor. The induction motor was used as a precaution against fires which could be caused by ignition of the evolving hydrogen. Sodium hydroxide solutions were put into the digestion flask and alloys were added while the solution was stirred.

Washing of Alloys.--The apparatus used for washing the alloys consisted of a 500 ml. round bottom flask which was fitted with a three hole rubber stopper. A stirrer was inserted through the stopper and attached to an electric motor. A container of

distilled water was placed above the flask and was attached to a glass tube passed through the stopper by means of a rubber hose. The glass tube reached the bottom of the flask and thus the catalyst slurry was swirled by the entering stream of water. The rate of water entering the flask was controlled by means of a valve attached to the distilled water container.

Another glass tube, placed barely through the stopper, was used to allow the wash water to run out the top of the flask. By altering the rate of stirring and the speed of fresh water entry, the apparatus was adjusted so that the catalyst was washed thoroughly but was not drawn off at the top.

Polarimeter.--The polarimeter used in the determinations of the optical activity of various d-limonene hydrogenation products was a Lippich half-shadow polarimeter. A sodium-vapor lamp was used as light source. The solutions to be tested were introduced into two decimeter glass tubes and placed in the instrument.

Procedure

Familiarization of Equipment.--Practice hydrogenations were run in order to learn the technique of high pressure hydrogenation. During these hydrogenations any leakages present were overcome as well as difficulties concerning the reading of the pressure gage.

Measurement of Materials.--The catalyst samples were transferred by means of a glass tube to the glass liners from bottles

containing catalyst under absolute ethyl alcohol. After the catalyst had settled, the excess alcohol was decanted. It was determined that drying the catalyst under a vacuum was not to be desired since the catalyst was thereby rendered less active. Why this should occur was not determined, but it was thought that there was a leak in the system so that the catalyst could have been poisoned by oxygen.

Liquid hydrogen acceptors were measured with a clean, dry five ml. pipette in all cases and placed in the glass liners directly upon the catalyst which was still damp with alcohol. Solid hydrogen acceptors were weighed on a balance and transferred to the glass liner after which the solvent was added to bring the total volume of catalyst, acceptor, and solvent to seven ml.

After the hydrogenation, the contents of the liner were transferred to a tared, sintered glass funnel. Liquid was removed by means of a vacuum aspirator and the catalyst and funnel dried and weighed to constant weight. In the few cases where the spent catalyst was pyrophoric, it was necessary to direct a stream of carbon dioxide over the catalyst during the filtering operation. It was enough to direct a stream of carbon dioxide into the balance a few seconds before closing the balance door and weighing the funnel and catalyst to prevent oxidation of the metal. If the funnel and catalyst were not completely dry, they were dried in a desiccator in an atmosphere of carbon dioxide.

Hydrogenation Technique.--After the liner had been charged with catalyst and hydrogen acceptor, and the top firmly placed on, it was lowered carefully into the bomb so that the vent hole was in such a position as to be upright when the bomb was placed in the shaker. The reaction vessel was lowered into a table vise and the head assembled. Unless the thrust bolts were screwed in gradually and symmetrically, the head would not be tight and hydrogen would leak from the bomb. No rates were accepted as good data if a leak, however small, was detected. If the leak were constant the rate would be too large. If the rate of leakage varied, as sometimes occured on continued shaking when one of the fixtures worked loose, the slope of the rate curve varied also. It was generally found that the rate of leakage varied when a leak was present and thus the leak could be detected. Constant leakages could only be discovered by applying a soap solution to the places susceptible to leaks and watching for any appearance of soap bubbles.

Superpressure tubing was used to connect the bomb to the hydrogen cylinder and the bomb was filled with hydrogen to a pressure of 1000 ± 50 psi. each time. The hydrogen line was disconnected and the bomb placed in the heating jacket. When a temperature of approximately 200° was to be used, the jacket was preheated, thus shortening the length of time necessary for the temperature to come to equilibrium. For temperatures near 100°, the voltage regulator was turned to the highest position

until the temperature was within 11° of the desired. This usually required approximately one hour. At this point, the voltage regulator was turned to a point where the desired temperature would eventually be obtained. It took approximately one hour more for the bomb to come to a constant temperature throughout, whereupon the shaking mechanism was started. Pressure readings were taken at regular time intervals and were accurate within a range of five psi.

The bomb liners, funnels, and other equipment were cleaned with sulfuric acid-potassium dichromate cleaning solution, rinsed and dried before each use. The bomb assembly was cleaned with methanol and acetone before each use.

Preparation of Catalyst

Raney Nickel.--The procedure used for the preparation of a Raney nickel catalyst to be used as a means of comparison of the rate of hydrogenation with various copper catalysts was that of Mozingo[8]. A solution of 380 g. sodium hydroxide was dissolved in 1500 ml. distilled water and placed in a four liter beaker. The beaker was equipped with an induction stirrer and was cooled in an ice bath. Three hundred g. Raney alloy was added in small portions during a period of 2.25 hours after which the ice bath was removed. The beaker attained room

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[8]R. Mozingo, Organic Synthesis, Coll. Vol. III (New York: John Wiley and Sons, Inc., 1955) p. 181.

temperature in 1.5 hours and was then put on a hot plate overnight. At infrequent intervals addition of water was necessary to keep the volume of solution approximately constant.

The sodium hydroxide solution was decanted and washed with 40 l. of distilled water. Approximately 1.5 l. portions were added, the slurry mixed and allowed to stand for three minutes after which the liquid was decanted and a fresh portion of distilled water added. The washing process was continued ten times after the solution had become neutral to perhydrion paper. The catalyst was washed three times with 200 ml. 95 per cent ethyl alcohol followed by three washings with absolute ethyl alcohol. The finished catalyst was stored under absolute ethyl alcohol in completely filled bottles which were tightly closed. The resulting catalyst was pyrophoric.

Raney Copper-1.--This catalyst was prepared from Devarda's alloy by grinding the commercial material in an agate mortor until the resulting powder was 100 mesh or finer. Thirty-seven and a half g. of alloy was added to a solution of 47.5 g. sodium hydroxide dissolved in 187 ml. distilled water. The alloy was added over a period of two hours so the solution would not foam so much that it would run over the top of the flask. This catalyst as well as all those following were prepared in the apparatus described in the section concerning the digestion of alloys. The digested alloy was brought to

room temperature and allowed to stand on a hot plate overnight. The washing process was essentially the same as that described for Raney nickel.

Raney Copper-1-A.--Devarda's alloy was ground to 200 mesh or finer by the use of the Mikro-Pulverizer previously described. The preparation of the catalyst was the same as that used for Raney Copper-1 except that the addition of the alloy required 3.5 hours. The washing was done by decantation of distilled water.

Raney Copper-2.--The alloy used in this and all other catalysts was prepared in this laboratory from the individual metals. The preparation of all alloys except those containing nickel, cadmium, and zinc was the same. The Handi-Melt was heated up until the melting point of copper (1080° C.) was reached. Both the copper and aluminum were added simultaneously and mixed thoroughly with carbon rods. After quenching the melts in cold water, they were broken up with a hammer and ground with the impact grinder.

R-Cu-2[9] was prepared from a 60 per cent copper, 40 per

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[9]The nomenclature used in the abbreviations of the catalyst names consists of several parts. The first letter "R" indicates that the catalyst is of a Raney type. This includes an indication both of the presence of aluminum and the procedure of digesting the alloy with sodium hydroxide. The second and third symbols indicate the metal or metals present besides aluminum. The first number indicates the batch number. Where several catalysts are prepared from the same alloy, the batch number of the first is used to indicate this. In these cases, the individual batch numbers of the other catalysts follow. Thus, if a catalyst contained only copper and aluminum and was the fourth catalyst to be made, it would be abbreviated "R-Cu-4". Other catalysts prepared from the same alloy might be designated "R-Cu-4-1" or "R-Cu-4-2", et cetera.

cent aluminum alloy. This and all the alloys yet to be discussed were ground to pass through a 200 mesh screen. The amount of alloy used in this digestion was 71 g. Ninety g. of sodium hydroxide was added to 355 ml. distilled water and the alloy was added to the base solution over a period of 1.75 hours. The remainder of the procedure was the same as R-Cu-1.

Raney Copper-3 and -4.--The alloy used for the preparation of R-Cu-3 was 50 per cent aluminum and 50 per cent copper by weight. R-Cu-4 was prepared from an alloy which was 60 per cent aluminum and 40 per cent copper. The amount of alloy used in each case was 90 g., and the amount of sodium hydroxide was 114 g. dissolved in 450 ml. distilled water. The addition of alloy took two hours with R-Cu-3 and five hours with R-Cu-4. Both were digested on a hot plate overnight and washed by decantation with distilled water.

Raney Copper-4-4.--This catalyst and any other copper catalyst having two numbers, the first of which is "4", were prepared from an alloy which contained 60 per cent aluminum and 40 per cent copper by weight. The procedure was essentially that of Adkins and Pavlic[10] for Raney nickel W-4 catalyst with a few modifications. One hundred fourteen g. sodium hydroxide was

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[10]H. Adkins and A. A. Pavlic, J. Am. Chem. Soc., 68, 1471 (1946); ibid., 69, 3039 (1947).

added to 450 ml. distilled water and cooled to 50° C. The addition of 90 g. alloy took 3.25 hours during which time the temperature was maintained at 50 ± 2° C.

The slurry was digested at 50° for 50 minutes and washed with the gravity washing apparatus described under the paragraph on washing of catalysts. The total washing time was 40 minutes at a rate of water addition of 250 ml. per minute. The washings were neutral to perhydrion paper after twenty minutes. The catalyst was washed three times by decantation with 95 per cent ethyl alcohol and twice with absolute ethyl alcohol after which it was stored in a bottle under absolute ethyl alcohol.

Raney Copper-4-6.--The preparation of this catalyst differed from R-Cu-4-4 in that it was intended that the temperature be kept between zero and ten degrees centigrade. This preparation was to be similar to that of Billica and Adkins[11] for Raney nickel W-6. However, when the addition was complete (1 hour), the solution was frozen. The sodium hydroxide solution in the flask was kept immersed in a dry ice-acetone bath for it was thought that the alloy could be added faster if more efficient cooling was attained. The frozen solution was slowly warmed to zero degrees, whereupon the reaction gained velocity and the material began to froth and foam and the container

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[11]H. R. Billica and H. Adkins, Organic Synthesis, Coll. Vol. III (New York: John Wiley and Sons, Inc., 1955) p. 176.

overflowed. At this point, tap water was added to stop the reaction and the material was washed with the gravity feed washing apparatus. The catalyst differed from the other copper catalyst in that it gave off bubbles of hydrogen when the bottle containing the completed catalyst was shaken.

Raney Copper-4-7.--This catalyst was prepared in the same manner as R-Cu-4-6, except that the reaction temperature of the digestion was actually kept between zero and ten degrees throughout the addition of alloy. The amount of alloy digested was reduced to 70 g. in order to shorten the digestion time. The addition of alloy took 1.25 hours and was facilitated by the addition of two ml. 1-octanol[11] which retarded excessive foaming. The slurry was digested at 20° C. and below for 45 minutes and then washed like R-Cu-4-4. This catalyst differed from all other copper catalysts prepared in that it was red in color. R-Cu-4-7, like Raney nickel, showed evidence of occluded or adsorbed hydrogen and was pyrophoric.

Raney Copper-4-8 and -4-9.--These catalysts were prepared according to the method used for R-Cu-4-4, except that two ml. R-Cu-4-4, 1-octanol was added in each case. The addition of R-Cu-4-8 alloy to the sodium hydroxide solution took only 1.25 hours because of the presence of the 1-octanol. For the same operation, R-Cu-4-9 alloy took 50 minutes.

Raney Copper-Nickel-1.--The preparation of this and all further

catalysts is similar to that used for R-Cu-4-4 except that 70 g. of the alloy was treated with 90 g. sodium hydroxide in 335 ml. distilled water, with the usual amount of 1-octanol. This particular catalyst was obtained from a 40 per cent nickel, 10 per cent copper, and 50 per cent aluminum alloy. It was believed that the alloy was not mixed well on preparation.

Raney Copper-Nickel-2, -3, and -4.--The alloys used for these catalysts were prepared in an induction furnace, since a higher temperature was required to melt the nickel than could be obtainable with the Handi-Melt furnace. The nickel was first melted, after which the copper was added and mixed thoroughly. This lowered the melting point of the nickel enough so that the aluminum would not be oxidized. The copper-nickel melt was cooled until it almost solidified before the aluminum was added.

All alloys used to make these catalysts contained 50 per cent aluminum. R-Cu-Ni-2 contained 25 per cent by weight of both nickel and copper. R-Cu-Ni-3 contained 40 per cent copper and 10 per cent nickel. R-Cu-Ni-4 contained the same percentages of metals as R-Cu-Ni-1, but proper mixing of the metals was attained and no oxidation of aluminum occurred. The time of addition of each of these alloys to the caustic was 30 minutes and the digestion period was one hour.

Raney Copper-Cadmium-1, -2, and -3.--All of the cadmium containing alloys contained 50 per cent aluminum. R-Cu-Cd-1 contained 10 per cent copper, 40 per cent cadmium; R-Cu-Cd-2

contained 25 per cent each of copper and cadmium; R-Cu-Cd-3 contained 40 per cent copper and 10 per cent cadmium. R-Cu-Cd-3 alloy was prepared a second time when the cadmium boiled out of the first aluminum-copper melt and oxidized at the temperature of the melt. By cooling down the melt of aluminum and copper until it was beginning to solidify, the addition of cadmium could be effected without oxidation.

Unlike all the rest of the alloys used in making the catalysts in this work, R-Cu-Cd-1 was not brittle but soft. The softness of this alloy made it difficult to break into pieces small enough for introduction into the Mikro-Pulverizer. The reason for this pliability was the large content of cadmium in this alloy.

All of the cadmium alloys were added to the sodium hydroxide solution in 30 minutes time. The procedures, including the temperature of digestion and the length of digestion, were the same as those used for R-Cu-4-4 except that 70 g. of the alloy was used, and the amount of sodium hydroxide was decreased proportionally.

All of the catalysts prepared in this work were black in color except R-Cu-4-7, which was red, and the cadmium alloys, which had particles of black and white in them. It was believed, as is discussed later, that the black particles were copper and the white were cadmium.

Raney Copper-Cadmium-4.--The alloy used for the preparation of this catalyst contained 60 per cent aluminum, 0.6 per cent

cadmium, and 39.4 per cent copper. The necessity of having the temperature of the copper-aluminum melt low enough so as not to oxidize the cadmium made the use of 60 per cent rather than 50 per cent aluminum a prerequisite. The preparation of the catalyst was identical with that of the previous cadmium catalysts.

Raney Copper-Zinc-1 and -2.--These alloys were prepared in the Handi-Melt in a manner similar to that used for cadmium, since zinc also oxidizes if the copper-aluminum melt is too hot.

Both of the alloys contained 45 per cent copper. R-Cu-Zn-1 contained 35 per cent aluminum and 20 per cent zinc, while R-Cu-Zn-2 contained 20 per cent aluminum and 35 per cent zinc. The preparation of these catalysts was identical in all respects to the procedure used for making the cadmium catalysts.

Raney Copper-Zinc-3.--Devarda's alloy, containing 45 per cent copper, 50 per cent aluminum, and 5 per cent zinc, was used in preparing this catalyst. The alloy was ground to 200 mesh or finer and the method of preparation is the same as that of the other zinc alloys mentioned above.

Determination and Analysis of Products

Determination of Catalyst Constituents.--The procedure used to determine the amount of aluminum[12] in catalysts R-Cu-4, R-Cu-4-4,

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[12]F. P. Treadwell and W. T. Hall, Analytical Chemistry, Vol. II (New York: John Wiley and Sons, Inc., 1948) p. 183.

R-Cu-4-6, and R-Cu-4-7 consisted in dissolving a weighed amount of catalyst in a minimum amount of concentrated nitric acid. Insoluble materials were filtered on ashless filter paper, ignited in a tared crucible, and weighed.

Aluminum hydroxide was precipitated with just enough ammonium hydroxide to make the solution basic. The solution was boiled for three minutes, filtered, and washed with two per cent ammonium nitrate solution. The precipitate was redissolved in nitric acid and reprecipitated with ammonium hydroxide. The aluminum hydroxide was filtered, washed, ignited, and weighed as aluminum oxide.

For determining copper in R-Cu-4, the alloy was dissolved as before in intric acid and the copper precipitated from hot solution with sodium hydroxide[13]. The copper was filtered, washed with hot water, ignited in a crucible, and weighed as cupric oxide.

A volumetric procedure[14] was used in the determination of copper in catalysts R-Cu-4-4, R-Cu-4-6, and R-Cu-4-7. The catalyst, when dissolved in nitric acid, was treated with concentrated sulfuric acid and evaporated down until fumes of sulfur trioxide were evolved. The insoluble residue was filtered. Ammonium hydroxide was added until the solution became very slightly basic. After boiling off the excess ammonia, an excess

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[13] Ibid., p. 65.

[14] Ibid., p. 612.

of acetic acid was added. Three g. C. P. potassium iodide was added and the solution titrated with standard sodium thiosulfate solution, starch solution being added toward the end of the titration.

Acetone.--The product from the hydrogenation of acetone was determined in two ways. The first method was distillation of the products, from which it was ascertained that isopropyl alcohol was the product of hydrogenation with Raney copper catalysts. It was not necessary to distill each product after it was ascertained that reduction did occur and that quantitative reductions were possible.

When other metals, such as cadmium or zinc, were included in the catalyst, a faster method of determining the per cent reaction was applied. Three solutions were required for this determination[15].

The first solution consisted of 50 ml. spectro grade pyridine and 0.625 ml. four per cent ethanolic bromphenol blue both dissolved in 2500 ml. 95 per cent ethyl alcohol. Seventy g. of C. P. hydroxylamine hydrochloride was dissolved in 320 ml. distilled water and this solution was diluted to two liters with 95 per cent ethanol to form the second solution. The last solution was a 0.5 N solution of sodium hydroxide in 90 per cent methanol from which the insoluble

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[15]W. M. D. Bryant and D. M. Smith, J. Am. Chem. Soc., 57, 57 (1935).

sodium carbonate coating the sodium hydroxide was filtered. The sodium hydroxide solution was standardized with dry potassium hydrogen phthalate.

The hydroxylamine hydrochloride was tested for excess hydrochloric acid by the method of Bryant and Smith[15]. Ten g. of hydroxylamine hydrochloride crystals should not require more than eight ml. 0.5 N sodium hydroxide solution to produce a neutral endpoint with bromphenol blue indicator. The end point is a blue to green color change. It was found that only one ml. of the sodium hydroxide solution was required to produce this color change.

For the determination of acetone, a sample of product was weighed in a flask into which 30 ml. hydroxylamine hydrochloride reagent and 100 ml. pyridine solution were introduced. According to Bryant and Smith, there must be a 50 per cent excess of hydroxylamine hydrochloride to ensure complete reaction according to the equation

$$CH_3COCH_3 + NH_2OH \cdot HCl \rightleftharpoons CH_3C(NOH)CH_3 + H_2O + HCl.$$

The fact that the pyridine is present to react with the hydrochloric acid, also ensures complete reaction, as well as preventing the hydrochloric acid formed from escaping as a gas.

Titration of the resulting mixture with 0.5 N sodium hydroxide indicates the amount of oxime produced. In this case the end point was a change in color from yellow to

green. Only the hydrochloric acid attached to pyridine is titrated. The per cent of acetone is readily calculated.

Liquid Hydrogen Acceptors.--The nitrobenzene products were treated with dilute hydrochloric acid solution to extract the aniline, after which the acid was neutralized to recover the aniline. Products from allyl alcohol, cinnamic acid, cyclohexene, and 2-pentene were determined by a bromine titration method which will be discussed fully in the next chapter.

The rest of the products, except those from mesityl oxide and d-limonene, were determined by fractional distillation alone. Besides the columns already described under the purification of acetone, an 18 inch Vigreux column was used for the distillation of small quantities of product.

The solid hydrogen acceptors will be discussed along with the results of their hydrogenation in the next chapter.

CHAPTER V

EXPERIMENTAL RESULTS

The Rate Curve.--The equation for a first order reaction,

$$\log \frac{p_o}{p} = \frac{kt}{2.303} ,$$

has already been derived. When $\log p_o/p$ is plotted against the time, t, a straight line of slope k/2.303 should result, and the rate constant can be calculated. For comparison with other work, it must be remembered that the rate constants given here must be multiplied by the volume of the reaction system.

Such deviations from simple first order kinetics as have been found by Gardner[1] for large differences in pressure, and by Cox[2] for product inhibition are overcome here by taking the initial rate of reaction over a pressure range of 100 to 300 psi.

In Fig. 1, a typical example is given for the curve encountered with the compounds hydrogenated in this study. It was ascertained by such curves as this that the rate was

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[1]L. E. Gardner, "The Catalytic Hydrogenation of Pyridine at High Pressures", Master's Thesis, Georgia Institute of Technology, 1952, p. 34.

[2]E. F. Cox, "The Catalytic Hydrogenation of Quinolines at High Pressures", Master's Thesis, Georgia Institute of Technology, 1951, p. 31.

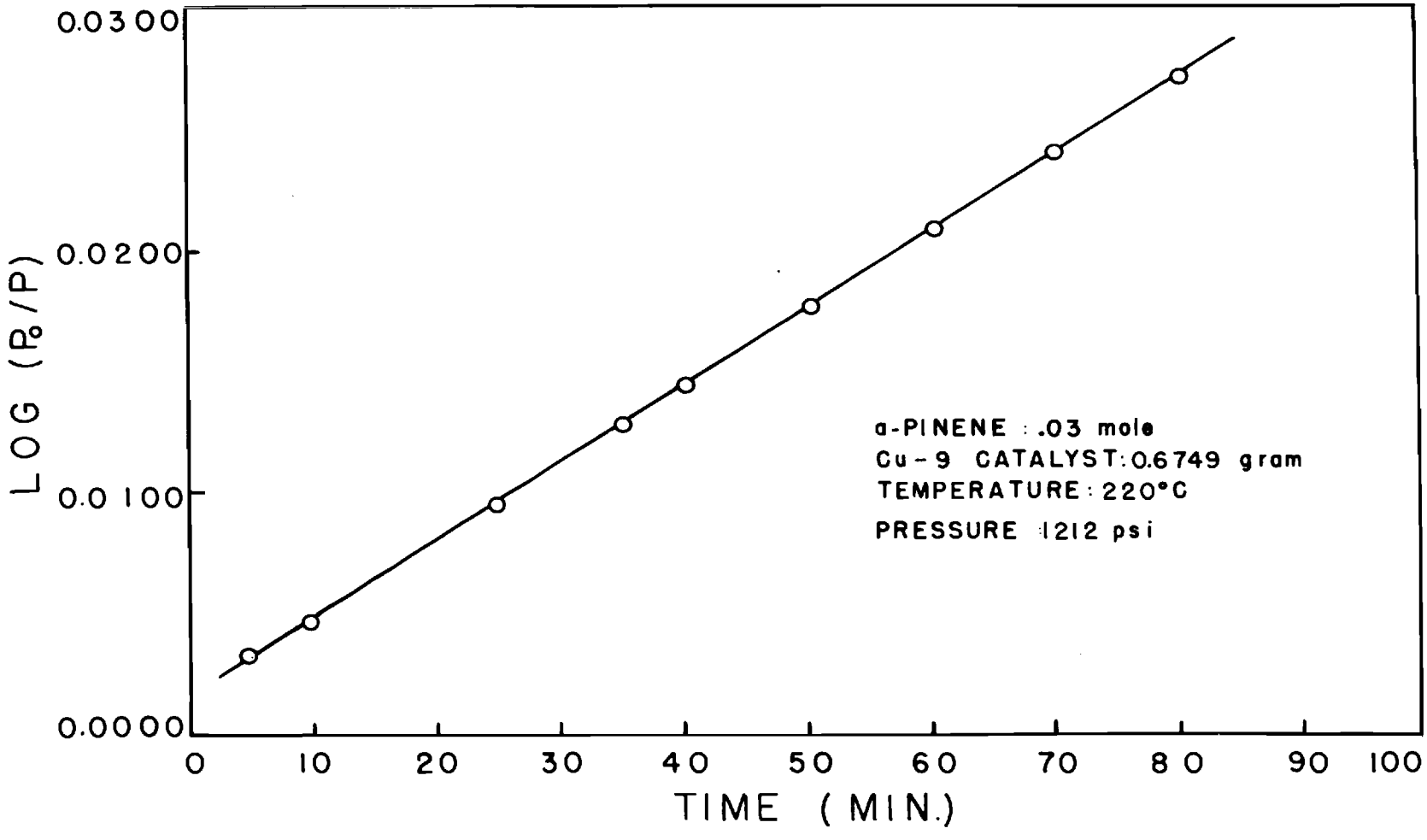

Figure 1. Sample Hydrogenation Curve.

first order with respect to hydrogen. These same kinetics have been found by Smith[3] and co-workers many times.

Where a rapid initial drop in hydrogen pressure was observed[4], the slope used to determine the rate constant was obtained without the use of the first few points. This steep initial drop never lasted over five minutes and since most of the pressure readings were made every five minutes for an hour or longer, it was usually only necessary to neglect the initial reading and the first one thereafter. Unless a straight line could easily be drawn through most of the points of the graph, the method of least squares was used in calculating the slopes of the lines.

Activation Energy.--The activation energies for the hydrogenations studied were calculated from a plot of log k versus 1/T, where k is the rate constant and T is the absolute temperature. The straight line obtained had a slope equal to $-E_a/2.303R$, where E_a is the apparent activation energy and R is the gas constant. The method of least squares was used to calculate the slopes of the graphs obtained in this work.

Fig. 2 is a typical example for the curve from which the activation energy is obtained. Tables 3 and 4 list the

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[3]H. A. Smith and J. A. Stanfield, J. Am. Chem. Soc., 71, 81 (1949).

[4]L. E. Gardner, "The Catalytic Hydrogenation of Pyridine at High Pressures", Master's Thesis, Georgia Institute of Technology, 1952, p. 37.

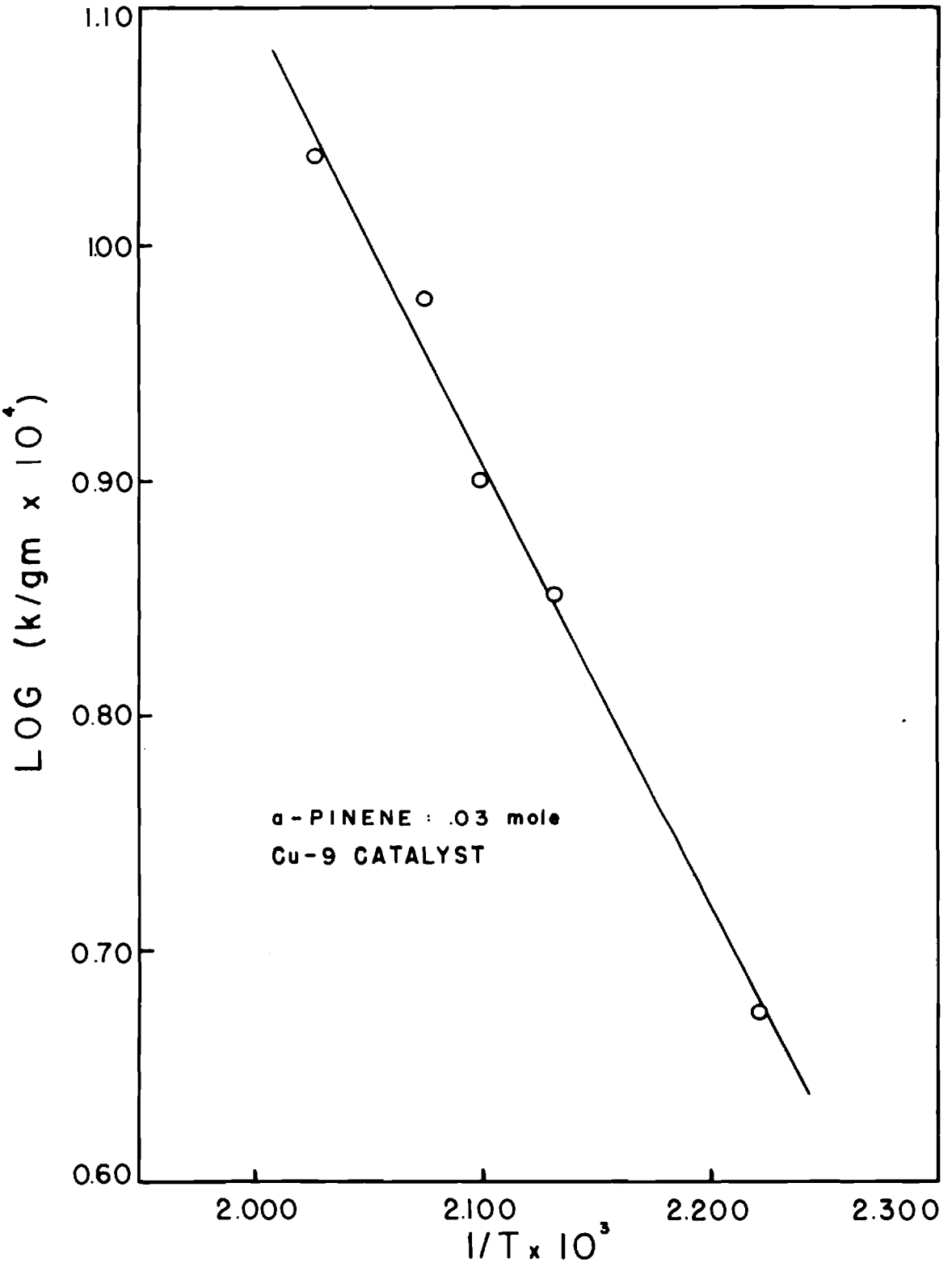

Figure 2. Energy of Activation Curve for α-pinene.

Table 3. Apparent Activation Energies for the Hydrogenation of Carbonyl Compounds.

Compound	Catalyst	Apparent Activation energy (kcal. mol^{-1}.)
Acetone	R-Cu-1	9.61
Acetone	R-Cu-1-A	9.74
Acetone	R-Cu-2	10.27
Acetone	R-Cu-4-4	8.90
Acetone	R-Cu-4-6	9.35
Acetone	R-Cu-4-7	7.87
Acetone	R-Ni	6.30
Benzaldehyde	R-Cu-4-9	6.57
Mesityl Oxide	R-Cu-4-8	8.46
Propionaldehyde	R-Cu-4-8	14.68

Table 4. Apparent Activation Energies for the Hydrogenation of Various Compounds.

Compound	Catalyst	Apparent Activation energy (kcal. mol^{-1}.)
Allyl alcohol	R-Cu-4-9	6.57
Butyronitrile	R-Cu-4-7	9.39
Cyclohexene	R-Cu-4-8	1.44
d-Limonene	R-Cu-4-9	5.31
Nitrobenzene	R-Cu-4	8.03
1-Nitropropane	R-Cu-2	11.00
1-Nitropropane	R-Ni	11.66
2-Pentene	R-Cu-4-9	4.30
α-Pinene	R-Cu-4-9	8.72
Styrene	R-Cu-4-8	10.72
Styrene (undistilled)	R-Cu-4-7	14.90

apparent activation energy values for the materials studied where the data was sufficient to make such a calculation.

The apparent activation energies for acetone are comparable to those found by van Mechelen and Jungers[5]. Those workers got values ranging from 8.5 to 11.9 kilocalories per mole for the hydrogenation of acetone with catalysts prepared from Devarda's alloy.

The explanation for the differences in activation energies observed with different catalysts is not definitely known. However, quantum mechanical calculations have been made which have shown that for the adsorption process, there is a high sensitivity of activation energies, and thus of rates, to the interatomic spacing at surfaces[6,7]. Furthermore, van Mechelen and Jungers[8], while finding different activation energies for different catalysts, found that the activation energies of the carbonyl group in various aliphatic ketones were the same for any given catalyst preparation.

For similar molecules, then, the activation energy should be similar for the same catalyst. The very low

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[5]C. C. van Mechelen and J. C. Jungers, Bull. soc. chim. Belges, 59, 597 (1950).

[6]S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes (New York: McGraw-Hill Book Co., 1941) p. 342.

[7]K. J. Laidler, Catalysis, Vol. I (New York: Reinhold Publishing Co., 1954) p. 237.

[8]C. C. van Mechelen and J. C. Jungers, loc. cit.

activation energy for cyclohexene (Table 4) cannot be explained in any simple way, since there is no way to compare it with other molecules of the same type which were hydrogenated with different catalysts.

Table 4 shows the activation energy for the hydrogenation of styrene with two different catalysts. However, it is expected that the activation energy should be higher when the catalyst is covered by a poison by an amount corresponding to the energy of adsorption of the poison. The reacting molecules, then, are required to expend a greater amount of energy to remove the poison molecules from the surface before they can be adsorbed and react. The poison present in the partially polymerized styrene may be either a polymerized molecule or a free radical.

Comparison of Copper Alloys.--Table 5 is a list of hydrogenation rates for acetone with various copper catalysts used in this work.

Of the various copper catalysts prepared by the method of Mozingo and digested overnight on a hot plate, (R-Cu-1 through R-Cu-4), the most active is the one which originally contained the most aluminum, R-Cu-4. Since it may be assumed that only the surface aluminum is leached in the digested catalyst, R-Cu-4 would still have the largest portion of aluminum by weight. Since the copper alone is the catalyst for hydrogenation, R-Cu-4 is definitely the most active.

Table 5. Effect of Catalyst Preparation on the Rate Constant for the Hydrogenation of Acetone at 127° C.

Catalyst	Alloy	Addition of Alloy	Digestion of Alloy	Rate Constant ($k \times 10^4$) ($min.^{-1}$ $g.^{-1}$)
Raney nickel	Raney alloy	2.25 hr. ice bath	Hot plate overnight	127.4
R-Cu-1	100 mesh Devarda's alloy	2 hr. ice bath	Hot plate overnight	18.07
R-Cu-1-A	200 mesh Devarda's alloy	3.5 hr. ice bath	Hot plate overnight	20.80
R-Cu-2	60% Cu-40% Al	1.75 hr. ice bath	Hot plate overnight	7.41
R-Cu-3	50% Cu-50% Al	2 hr. ice bath	Hot plate overnight	21.63
R-Cu-4	40% Cu-60% Al	5 hr. ice bath	Hot plate overnight	25.12
R-Cu-4-4	40% Cu-60% Al	3.25 hr. 50 ± 2°	50° for 50 min.	60.95
R-Cu-4-6	40% Cu-60% Al	1 hr. 0.10°	None	42.86
R-Cu-4-7	40% Cu-60% Al	1.25 hr. 0-10° 1-octanol	20° and below, 45 min.	87.10
R-Cu-4-8	40% Cu-60% Al	1.25 hr. 50 ± 2° 1-octanol	50° for 1 hr.	57.28
R-Cu-4-9	40% Cu-60% Al	50 min. 50 ± 2° 1-octanol	50° for 1 hr.	75.33

Smith, Bedoit, and Fuzek[9], in a study of Raney nickel hydrogenations of d-limonene, conclude that differences in the original alloy result in differences in activity of the catalyst. They also state that the method of addition of the alloy to sodium hydroxide solution, the time or temperature of the digestion beyond a minimum of one hour at 50 degrees, or washing method have no great effect on the activity of the catalyst.

However, Table 5 shows that in this work it was found that the same alloy digested at 20° is more active than one digested at 50°, or one digested on a hot plate overnight. Smith, Bedoit, and Fuzek digested one alloy at 20° for one hour, but followed this by a digestion overnight on a hot plate, so that this catalyst cannot be compared with others which were digested for one hour at 50° unless it is kept in mind that the digestion, in reality, was overnight on a hot plate. It thus appears that the digestion temperature does have a bearing on the activity of the catalyst surface for copper, just as Adkins and Billica[10] claim for nickel. While the differences in the rates for some of the copper alloys are not great, they are consistent with this idea.

In fact, whenever the time of addition of alloy to the

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[9]H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, J. Am. Chem. Soc., 71, 3769 (1949).

[10]H. Adkins and H. R. Billica, ibid., 70, 695, (1948).

sodium hydroxide or the time of digestion is lengthened, or the temperature increased in these processes, the activity of the catalyst prepared from a given alloy seems to decrease. R-Cu-4-6 is an exception to this, since the digestion was far from complete and hence not much aluminum was removed, and there was more aluminum left in the catalyst to be weighed as active catalyst.

The particle size of the alloy will change the surface area of the catalyst, but the surface area does not necessarily effect the activity of individual catalysts[11]. The rate of hydrogenation with R-Cu-1 and R-Cu-1-A is not appreciably different even though the alloys were ground to 100 and 200 mesh, respectively. This does not mean that the amount of surface area of any given catalyst is not important, for the rate is directly proportional to it as has already been explained in Chapter II. Smith, Bedoit, and Fuzek also found that the surface area decreases as the rate decreases with aging of the catalyst.

The results of the catalyst metal determinations may be found in Table 6. They show very low percentages of aluminum remaining after digestions at 50° for 50 minutes and for digestions on a hot plate overnight, as is the case with R-Cu-4-4 and R-Cu-4, respectively. Perhaps the aging of the catalyst, whatever that entails besides decreasing the catalyst

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[11]H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, loc. cit.

Table 6. Composition of Catalysts[12]

Catalyst	% Aluminum	% Copper	% Insoluble material
R-Cu-4	4.87	93.20	1.62
R-Cu-4-4	5.48	93.48	1.00
R-Cu-4-6	49.46	47.60	0.00
R-Cu-4-7	34.30	65.96	0.00

[12]The values listed in the table are the average values of two determinations.

surface area, is speeded up by a long digestion at temperatures close to that of boiling water as occurs in the digestion on a hot plate. Catalyst R-Cu-4-7 was the most active, yet did not have as much of the aluminum removed as R-Cu-4-4.

Aging of Catalysts.--Table 7 shows how the rates of various catalysts decrease with time. The effect of aging with time for R-Cu-4-6 and R-Cu-4-7 is a linear drop in the rate constant. The rates of these catalysts would be the same fourteen months after their preparation if the present rate of loss of activity continued. R-Cu-2 is entered in the table to show that eventually the rate becomes zero, or at least negligible, at the temperatures at which the reaction with fresh catalyst is successful.

R-Cu-4 lost its activity more quickly because of the evaporation of the alcohol from the bottle in which it was contained during the first 3.6 months. The catalyst did not dry out completely, but was only damp with the alcohol. The rate of hydrogenation using this catalyst dropped quickly and then leveled off.

Smith, Bedoit, and Fuzek found that the aging of Raney nickel was at first rapid and then leveled off. The Raney nickel lost 33 per cent of its activity in approximately ten days. Raney copper catalysts, on the other hand, lost approximately one-third of their reactivity in 4.95 months.

Hydrogenation of d-Limonene.--The distillation of the hydrogenation products of d-limonene, where the hydrogen pressure

Table 7. Effect of Aging of Catalyst on the Rate of Hydrogenation of Acetone.

Catalyst	Temperature (° C.)	Rate Constant ($k \times 10^4$) ($min.^{-1}$ $g.^{-1}$)	Time (months)
R-Cu-2	121	6.03	0
R-Cu-2	121	0.00	18.5
R-Cu-4-4	121	53.33	0
R-Cu-4-4	121	23.97	3.6
R-Cu-4-4	121	22.64	6.0
R-Cu-4-4	121	12.95	12.0
R-Cu-4-6	122	37.16	0
R-Cu-4-6	122	20.01	7.6
R-Cu-4-6	122	10.00	12.0
R-Cu-4-7	122	77.09	0
R-Cu-4-7	122	38.49	7.5
R-Cu-4-7	122	16.80	11.8

drop was enough to hydrogenate 30 per cent of one of the two double bonds in the compound, gave no p-menthane (b.p. 168.0° C.), but gave about 40 per cent d-carvomenthene (b.p. 178.80° C. corr.) along with 60 per cent unreacted starting material. The boiling point of d-carvomenthene reported in the literature by Smith, Fuzek, and Meriwether[13] is 179.0°.

As a further means of following the reaction, hydrogenations were made for various uptakes of hydrogen. Table 8 shows the volume of five per cent bromine in acetic acid absorbed in each hydrogenation along with the values of per cent reacted calculated both from the amount of bromine solution decolorized[14] and from the pressure drop of hydrogen during the run.

The polarimeter readings were determined by distilling any alcohol present from the product and then dissolving two ml. of the product in 25 ml. absolute ethyl alcohol. These solutions were introduced into two decimeter polarimeter tubes and placed in the polarimeter where the optical rotations were observed. It was not desired to convert the polarimeter readings into specific rotation, but only to follow the loss in activity of the product as the compound was hydrogenated.

A plot of the polarimeter reading versus the per cent

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[13]H. A. Smith, J. F. Fuzek, and H. T. Meriwether, J. Am. Chem. Soc., 71, 3765 (1949).

[14]K. Uhrig and H. Levin, Ind. Eng. Chem., Anal. Ed., 13, 90 (1941).

Table 8. Polarimeter Readings for Partially Hydrogenated d-Limonene.

Hydrogen pressure loss (psi.) during hydrogenation	Bromine titre[15]	Per cent reacted (bromine titre)	Per cent reacted (pressure drop)	Polarimeter reading[15]
None	4.25	0	0	13.30
86	3.75	11.8	12.2	12.40
250	2.75	35.3	33.6	12.00
260	2.60	38.8	37.6	11.75
312	2.23	48.5	45.9	11.60
320	2.25	47.0	47.0	11.30
517	1.15	75.0	75.7	5.35

[15]The figures for the bromine titre are the average of two determinations; those for the polarimeter readings are the average of five.

reacted gives a straight line which changes slope at 50 per cent reaction, indicating a two step reaction[13]. The first step is the hydrogenation of the exo-bond of d-limonene producing d-carvomenthene, which then is reduced further and more slowly to p-menthane. If the hydrogen reduced both bonds simultaneously, a straight line would be produced from the activity of pure d-limonene at zero per cent reduction to zero activity at 100 per cent reduction, instead of the broken line observed. If the endo bond was reduced first, there would be a total loss in activity when the hydrogenation was 50 per cent completed.

Part of the product from the run which had a 312 psi. pressure drop of hydrogen (48.5 per cent reacted according to the bromine titration) was used in determining the rate of hydrogenation of d-carvomenthene in Table 12. This is the rate of hydrogenation of the endo bond of d-limonene. The rate of hydrogenation of d-limonene given in this table is calculated from the rate at other temperatures by means of the Arrhenius equation.

Hydrogenation of Mesityl Oxide.--From the first hydrogenation of mesityl oxide, distillation gave a fraction which boiled at 137.5-8.0° C. (uncorrected). The rate of this first hydrogenation was anomalous in that it was 46.09 $min.^{-1}$ $g.^{-1}$, while the rate calculated from the Arrhenius equation, using all other rates determined, showed that the rate would be 20.99 $min.^{-1}$ $g.^{-1}$ at the same temperature. This first

hydrogenation was the only one which gave anomalous results such as this.

In order to clarify further the results of the hydrogenation of mesityl oxide, distillations were run on the products of several runs. Table 9 gives the possible products along with their boiling points and refractive indices.

One of these distillations revealed that 4-methyl-2-pentanone was a main product, since a large fraction boiled at 114.5-5.0° C., n_d 1.3958. This material did not decolorize bromine solution.

When the hydrogen absorbed was sufficient to hydrogenate the double bond to an extent of 55.3 per cent, considering the carbonyl group unreduced, 4-methyl-2-pentanone (b.p. 122.4; n_d 1.3965-1.4019) was formed in 38 per cent yield; 4-methyl-2-pentanol in 6.8 per cent yield; and there was 55.2 per cent unreacted mesityl oxide (b.p. 128-30; n_d 1.4448) remaining. The yield of 4-methyl-2-pentanol was determined by treating the product with 90 per cent sulfuric acid and distilling the unsaturated materials formed. The loss in pressure of hydrogen required to hydrogenate the compound completely, both carbonyl group and double bond, is roughly calculated from the amount of hydrogen necessary to reduce completely a known amount of acetone. It had been previously found that 100 psi. hydrogen is required to reduce 0.0136 moles of acetone with the apparatus used in this work.

The amount of hydrogen used up in another hydrogenation

Table 9. Physical Constants
Possible Mesityl Oxide Products.

Compound	Boiling Point[16] (° C.)	Refractive Index[16]
Mesityl oxide	128.7-30.0	1.4446
4-Methyl-2-pentanone	117, 115-8	1.3959
4-Methyl-2-pentanol	131.4	1.4087
4-Methyl-3-penten-2-ol	138-40	1.4377

[16]N. A. Lange, Handbook of Chemistry, 7th ed. (Sanduskey, Ohio: Handbook Publishers, Inc., 1949).

was enough to hydrogenate all but eight per cent of the double bond, considering the carbonyl group to be untouched. The distillation revealed 86 per cent 4-methyl-2-pentanone, 9.5 per cent 4-methyl-2-pentanol, and 4.5 per cent mesityl oxide.

Still another hydrogenation was made in which the hydrogen pressure drop would be enough to hydrogenate all of the double bond and half the carbonyl group. Distillation of this product gave a yield of 55 per cent of the 4-methyl-2-pentanol and 45 per cent of 4-methyl-2-pentanone. The rate curve for this hydrogenation showed a break in the slope at 50 per cent reaction, after which the rate was slower. The results indicate that the double bond is reduced first, followed by reduction of the carbonyl group. This is contrary to what might be expected from observation of the hydrogenations of compounds possessing either one, but not both, of these groups. In these cases, it was found that the carbonyl group is hydrogenated at a greater rate than the ethylene linkage.

Mesityl oxide has been hydrogenated by Covert, Connor, and Adkins[17] to 4-methyl-2-pentanone in 95 per cent yield with a reduced nickel catalyst. Their work shows also that the double bond is preferentially hydrogenated. Lebedev, Kobliansky, and Yakubchik[18] also studied the hydrogenation of

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[17] L. W. Covert, R. Connor, and H. Adkins, J. Am. Chem. Soc., 54, 1651 (1932).

[18] S. V. Lebedev, G. G. Kobliansky, and A. O. Yakubchik, J. Chem. Soc., 127, 417 (1925).

mesityl oxide while investigating compounds with double bonds, and found that conjugation of the double bond with carbonyl groups increased the rate of hydrogenation of the double bond. Table 12 shows the rate of hydrogenation of the double bond of mesityl oxide along with that of styrene, where conjugation also occurs, and other compounds where there is no conjugation. Table 10 gives the rate of hydrogenation of the carbonyl group of the half-reacted mesityl oxide, that is, 4-methyl-2-pentanone.

Comparison of Compounds.--Table 10 lists the rate constants per gram of catalyst for the carbonyl compounds studied in this work.

The carbonyl compounds are readily hydrogenated completely, the yield depending solely on the recovery of the product from the liner. The rates are generally faster for the carbonyl group than for other groups if these groups alone are present in the compound.

The dates of each experiment are also given in Table 10 along with the calculated initial rate constant. This corrected rate constant is the constant which would be found if the catalyst were freshly prepared. The acetone determinations were made when the catalyst was first prepared and, therefore, those dates are used in determining the new rate constants. In all cases where corrected rate constants were calculated for R-Cu-4-4, it was assumed that the aging caused a linear drop in rate for this catalyst also. The reason this can be

Table 10. Rate Constants for the Hydrogenation of Carbonyl Compounds

Compound	Catalyst	Temperature (° C.)	Date	Rate Constant ($k \times 10^4$) ($min.^{-1}$ $g.^{-1}$)	Rate Constant (corrected for aging of catalyst)
Acetone	R-Cu-1	127	5/8/54	18.07	
Acetone	R-Cu-1-A	127	6/4/54	20.80	
Acetone	R-Cu-2	127	7/15/54	7.41	
Acetone	R-Cu-3	127	7/24/54	21.63	
Acetone	R-Cu-4	127	9/7/54	25.12	
Acetone	R-Cu-4-4	127	1/19/55	60.95	
Acetone	R-Cu-4-6	127	1/26/55	42.86	
Acetone	R-Cu-4-7	127	1/31/55	87.10	
Acetone	R-Cu-4-8	127	5/12/55	57.28	
Acetone	R-Cu-4-9	127	7/27/55	75.33	
Acetone	R-Ni	127		127.4	
Benzaldehyde	R-Cu-4-9	127	8/16/55	30.90	32.36
Benzaldehyde (contaminated)	R-Cu-4-9	127	8/1/55	5.11	5.16
Mesityl oxide	R-Cu-4-9	127	9/19/55	55.38	62.72
Mesityl oxide	R-Cu-4-9	174	9/19/55	77.28	87.52
Mesityl oxide (50 % reacted)	R-Cu-4-9	174	9/19/55	17.70	20.05
Propionaldehyde	R-Cu-4-8	127	7/14/55	23.29	26.89

done is that the only corrections necessary were for nitrobenzene (Table 11), after an aging of only approximately one-half a month, and for compounds in Table 14 where the aging was over a year. After less than one month, the catalyst still had alcohol covering it and the aging would be linear up until that time. Furthermore, the catalyst after 12 months had a rate that was 20 per cent of its original rate, which holds true for the other catalyst as well (Table 7).

Benzaldehyde, when freshly vacuum distilled just before use, is free from benzoic acid and gives a rate of 32.36 $min.^{-1}$ $g.^{-1}$ (corrected). Hydrogenations were at first conducted with benzaldehyde which had been distilled once and stored in a refrigerator. The contamination of benzaldehyde by benzoic acid lowers the rate constant at 127° to 5.16 $min.^{-1}$ $g.^{-1}$ (corrected). When pure, benzaldehyde gave benzyl alcohol (b.p. 204.7°) in quantitative yields.

Mesityl oxide hydrogenates to give as an initial product, 4-methyl-2-pentanone, the rate for which is 62.72 $min.^{-1}$ $g.^{-1}$ (corrected) at 127°. When the hydrogenation is continued until complete reduction, the rate of reaction is slower after 50 per cent total hydrogenation. At 174°, the rate of hydrogenation of the double bond was 87.52 $min.^{-1}$ $g.^{-1}$ (corrected), while the rate of hydrogenation of the carbonyl linkage of the intermediate product was 20.05 $min.^{-1}$ $g.^{-1}$ (corrected).

It may be seen from Table 10 that propionaldehyde is less easily reduced than acetone with R-Cu-4-8. Propionaldehyde gave n-propyl alcohol (b.p. 97.4°) in quantitative yields.

The results for the hydrogenation of nitrobenzene with various catalysts (Table 11), when compared with the results for acetone and various catalysts indicate, in general, that the most active catalyst with one compound is the most active with the other. Thus, in the order of increasing activity with both compounds, the catalyst are R-Cu-2, R-Cu-1-A, R-Cu-3, R-Cu-4 and R-Cu-4-6, and R-Cu-4-4. Therefore, in comparing the rates given in Tables 10, 11 and 12, the individual catalyst should be kept in mind. R-Cu-4 and R-Cu-4-8 are about the same in activity, both being less than R-Cu-4-7 and R-Cu-4-9, which are about the same in activity.

Nitro groups are less readily hydrogenated than carbonyl groups, as can be seen by comparing the rates for 1-nitropropane with propionaldehyde, and the rates for nitrobenzene with benzaldehyde. However, yields of nitropropane were quantitative and yields for nitrobenzene were almost so at higher temperatures. Raney nickel reduced 1-nitropropane at a much greater rate than did any of the copper catalysts. There was not such a great difference in the hydrogenation of nitrobenzene with these catalysts, although nickel still was more active. The products formed from these hydrogenations

Table 11. Rate Constants for the Hydrogenation of Miscellaneous Compounds

Compound	Catalyst	Temperature (° C.)	Date	Rate Constant ($k \times 10^4$) ($min.^{-1}$ $g.^{-1}$)	Rate Constant (corrected for aging of catalyst)
Butyronitrile	R-Cu-4-7	223	2/23/55	9.39	9.89
Butyronitrile	R-Cu-4-7	127	2/23/55	1.08	1.14
Nitrobenzene	R-Cu-1-A	127	2/9/55	2.03[19]	4.30
Nitrobenzene	R-Cu-2	127	2/9/55	2.37	4.23
Nitrobenzene	R-Cu-3	127	2/7/55	3.39	5.82
Nitrobenzene	R-Cu-4	127	2/7/55	4.51	6.73
Nitrobenzene	R-Cu-4-4	127	2/8/55	12.60	13.32
Nitrobenzene	R-Cu-4-6	127	2/7/55	5.48	5.72
Nitrobenzene	R-Ni	127	2/9/55	89.1	
1-Nitropropane	R-Cu-2	127	2/14/55	2.99[19]	5.56
1-Nitropropane	R-Cu-4-7	127	2/15/55	16.50	17.06
1-Nitropropane	R-Ni	127	2/16/55	5890	

[19]All the rates for nitrobenzene were calculated from other temperatures using 8.03 kilocalories, the value for R-Cu-4, as the activation energy; the rate of hydrogenation of 1-nitropropane with R-Cu-4-7 was calculated using an activation energy of 11.00, the value found for R-Cu-2.

were determined by treating them with dilute hydrochloric acid solution. The aniline was then recovered by neutralizing the acid layer. The boiling point of the recovered aniline was 184.2° C. (corr.). The product from the 1-nitropropane runs were easily fractionated.

The product from the hydrogenation of butyronitrile was distilled giving butylamine as a fraction (b.p. 76-8° C. corr.). The hydrogenation of this compound was slow and required a temperature of 220° for appreciable rates to occur.

The hydrogenations of unsaturated materials are listed in Table 12. The products of these runs were determined in two ways. Products from α-pinene and styrene were fractionally distilled. The product of hydrogenation of α-pinene, i.e., pinane, has a boiling point of 166.0°, and the yields were quantitative when the calculation was based on the amount of hydrogen uptake. Styrene gave a quantitative yield of ethylbenzene (b.p. 136.3° corr.).

The other method used to determine the product of hydrogenation of unsaturated compounds was the method of Uhrig and Levin[20]. Five per cent bromine in acetic acid was used to titrate the products. Similar titres were obtained for the unreacted material and thus a percentage was determined. Table 13 gives the average titre for the compounds determined

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[20]K. Uhrig and H. Levin, Ind. Eng. Chem., Anal. Ed., 13, 90 (1941).

Table 12. Rate Constants for the Hydrogenation of Unsaturated Compounds.

Compound	Catalyst	Temperature (° C.)	Date	Rate Constant ($k \times 10^4$) (min^{-1} $g.^{-1}$)	Rate Constant (corrected for aging of catalyst)
Allyl alcohol	R-Cu-4-9	127	9/6/55	33.88	37.11
Carvomenthene (50% hydrogenated d-limonene.)	R-Cu-4-9	194	10/31/55	6.87	8.56
Cinnamic acid (0.8958 g. in ethanol solvent)	R-Cu-4-8	207	6/11/55	1.50	1.61
Cyclohexene	R-Cu-4-8	127	5/27/55	3.84	3.96
Cyclohexene	R-Cu-4-8	194	5/27/55	4.68	4.83
d-Limonene	R-Cu-4-9	127	8/24/55	4.98	5.33
d-Limonene	R-Cu-4-9	194	8/24/55	12.92	13.83
Maleic anhydride (n-hexane solvent)	R-Cu-4-8	160	6/27/55	3.09	3.43
Mesityl oxide	R-Cu-4-9	127	9/19/55	55.38	62.72
2-Pentene	R-Cu-4-9	127	8/4/55	10.06	10.21
α-Pinene	R-Cu-4-9	127	8/30/55	1.40	1.50
α-Pinene	R-Cu-4-9	194	8/30/55	6.71	6.97
Styrene	R-Cu-4-8	127	7/15/55	328.9	378.9
Styrene (undistilled)	R-Cu-4-7	127	3/22/55	242.6	278.8
Styrene (undistilled)	R-Ni	127	4/5/55	398.1	

Table 13. Titration of Products from Unsaturated Acceptors with 5 Per cent Bromine-Acetic Acid.

Compound	Titre	% Reaction (Bromine titration)	% Reaction (Hydrogen pressure loss)
Allyl alcohol	7.73	0	0
Allyl alcohol product	5.10	34.1	35.3
Cinnamic acid product	0.00	100	100
Cyclohexene	4.87	0	0
Cyclohexene product	4.13	15.2	17.1
2-Pentene	5.31	0	0
2-Pentene product	3.78	28.9	27.4

in this way. The per cent reaction is not the maximum possible, but just the yield after about two hours. Total hydrogenation was found to give almost quantitative yields of product.

Table 12 shows that the exo double bond of d-limonene had a rate of 13.83 $min.^{-1}$ $g.^{-1}$ (corr.), whereas the endo bond has a rate of 8.56 which may be compared with the rate of d-pinene with the same catalyst of 6.97. Cyclohexane was run with R-Cu-4-8 which was less active than R-Cu-4-9, the corrected rate constant being 5.33 at 194°. Thus for R-Cu-4-9, the rate would have been comparable to the endo double bonds in d-pinene and d-limonene.

Straight chain olefins, such as 2-pentene and allyl alcohol, have a greater rate than ring compounds. Where the double bond is conjugated with a benzene ring as in styrene, and with a carbonyl group as in mesityl oxide, the rate is increased.

An impure sample of 1,3-cyclohexadiene showed no detectable reaction. Smith and Meriwether[21] have previously shown that cyclohexadiene is less readily hydrogenated than cyclohexane.

Benzene has never been found to be readily hydrogenated by copper[22] and was not hydrogenated by these copper catalysts

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[21]H. A. Smith and H. T. Meriwether, J. Am. Chem. Soc., 71, 413 (1949).

[22]P. W. Reynolds, J. Chem. Soc., 1950, 265.

either. It could thus be used as a solvent.

Effect of Added Sodium Hydroxide.--Compounds that could have acid impurities were found to hydrogenate very slowly or not at all. Thus, benzaldehyde was less reactive unless it was hydrogenated immediately after vacuum distillation. Other compounds which reacted slowly when not completely pure were ethyl oleate, 2-pentene, and 2-methyl-2-butene. Fumaric acid and cinnamic acid did not react. Cinnamic acid in the presence of ethyl alcohol gave only ethyl cinnamate as a product. Thus it seemed that the presence of either an inorganic or organic acid deterred the reaction.

2-Pentene was found to react readily when dried over sodium hydroxide before use, thus supporting the idea of acid retardation. Another indication of this was that the catalysts frequently lost weight after the hydrogenation of these compounds. It is likely that acid present tends to dissolve some of the aluminum remaining on the surface of the catalyst, leaving the catalyst, originally black, a red color. The catalysts turned red after reaction of all the compounds which might have acids present as impurities. Nitrobenzene was an exception. In this case the catalyst was blacker at the end of the reaction than at the beginning. R-Cu-4-7, for instance, was reddish-black in color before reaction, black after reaction. This effect was thought to be due to the oxidation of the copper surface to copper oxide by the nitrobenzene. It was determined that this oxide surface was easily rinsed off

the catalyst by treatment with dilute mineral acid.

The addition of sodium hydroxide, then, should increase the rates of reaction of those compounds which contain acid impurities, since it was earlier determined that leaching the catalyst with acid gave a catalyst with no activity. In a previous experiment, Devarda's alloy had been digested with very dilute nitric acid and washed thoroughly. This catalyst did not hydrogenate acetone.

Van Mechelen and Jungers[23] report that the addition of up to 0.03 g. of sodium hydroxide increased the rate of hydrogenation of 100 ml. acetone with 1 g. Raney nickel, but that greater amounts of base decreased the rate. In the present work on the effect of added sodium hydroxide, amounts of sodium hydroxide greater than this have been used. Any increase in rate, then, is due to the neutralization of acid present rather than an effect on the catalyst itself, as is the case when up to 0.03 g. sodium hydroxide is added.

Table 14 gives the results found on addition of sodium hydroxide to various compounds. With cinnamic acid, the same effect was found as was found with impure benzaldehyde; that is, the rate was smaller when free organic acid was present. By preparing the sodium salt of cinnamic acid, the material was readily reduced. The rate of hydrogenation is greater

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[23]C. C. van Mechelen and J. C. Jungers, Bull. soc. chim. Belges, 59, 597 (1950).

Table 14. Effect of Sodium Hydroxide on Reaction Rate.

Compound	Catalyst	Moles sodium hydroxide	Rate Constant (k x 10^4 $min.^{-1}$ $g.^{-1}$)	Temperature (^{o} C.)	Date
Acetone	R-Cu-4-4	0	12.95 (62.27)[24]	121	1/22/56
Acetone	R-Cu-4-4	0.0064	9.31 (56.71)	121	2/10/56
Cinnamic acid (0.0065 mole in ethanol)	R-Cu-4-8	0	1.50 (1.61)	207	6/11/55
Cinnamic acid (0.0067 mole in methanol)	R-Cu-4-4	0.0034	2.33 (11.20)	197	1/20/56
Cinnamic acid (0.0068 mole in water)	R-Cu-4-4	0.0069	6.16 (29.66)	197	1/29/56
Cinnamic acid (0.0068 mole in water)	R-Cu-4-4	0.0116	6.20 (29.81)	197	1/21/56
Cyclohexene	R-Cu-4-8	0	4.53 (4.68)	170	5/27/55
Cyclohexene	R-Cu-4-4	0.0069	2.81 (13.50)	170	1/23/56
Nitrobenzene	R-Cu-4-4	0	41.69 (43.61)	191	2/8/55
Nitrobenzene	R-Cu-4-4	0.0077	7.28 (36.65)	191	1/24/56

[24]The figures in parentheses are the rate constants corrected for aging.

with R-Cu-4-4 and added sodium hydroxide, even though the catalyst was not as effective as R-Cu-4-8. It may be seen in Table 14 that addition of sodium hydroxide need not be more than is necessary to form the sodium salt, the rate remaining constant after this.

Addition of sodium hydroxide to cyclohexene enhanced the corrected rate, as can be seen from the table. The less active catalyst, R-Cu-4-4, would be expected to give a rate smaller than was observed with R-Cu-4-8. These results indicate the presence of an acid impurity.

Addition of sodium hydroxide to nitrobenzene appears to decrease the rate more than is to be expected by the aging of the catalyst. Sodium hydroxide, like acids, leaches away more aluminum when present at 191°. The catalyst was red in the determinations with nitrobenzene and cyclohexene and may have been somewhat deactivated. This appears to be so with nitrobenzene and acetone. It may be stated that while sodium hydroxide may or may not have an ill effect on the rate, it does not accelerate the rate with nitrobenzene and acetone. The leaching of aluminum should tend to increase the rate by decreasing the weight of catalyst after reaction, since the observed rate is divided by the weight of spent catalyst. Thus, it appears that oxidation of the copper surface is the reason for the slow hydrogenation of nitrobenzene.

Comparison of Rates with Different Amounts of Catalyst.--The rate of hydrogenation of liquids has always been found to vary

directly with the amount of catalyst. In Table 15 is a list of various catalyst weights along with the rate constants. It can be seen that the rate constant increases as the amount of catalyst decreases, until a certain weight is reached, below which the rate is constant.

This maximum weight of catalyst varies from catalyst to catalyst. The explanation for this is that the catalyst must be shaken loose from the bottom of the liner so that diffusion of unreacted molecules to the catalyst and reacted particles away from the catalyst is not important. If the catalyst sticks to the bottom of the liner, as has sometimes been found when large weights of catalysts are present, equilibrium conditions are not obtained and the lowered rates show that the effective amount of catalyst is lower than the real amount. Some catalysts pack closer and tighter than others and the shaking apparatus is not fast enough to shake larger quantities of the more densely packed catalyst loose. Thus it is shown in Table 15 that 2.1700 g. of R-Cu-Ni-3 is not too much to affect the rate, but 1.882 g. of R-Cu-1-A affects the rate adversely.

Difficulties encountered in this manner have been overcome by using between one-half and one g. of catalysts for all rate determinations recorded in other tables.

Smith, Bedoit and Fuzek[25] found the same effect from

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[25]H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, J. Am. Chem. Soc., 71, 3769 (1949).

Table 15. Relation Between Catalyst Weight and Rate Constant

Compound	Catalyst	Weight of catalyst (g.)	Rate Constant ($k \times 10^4$) ($min.^{-1}$ $g.^{-1}$)	Temperature (^{o} C.)
Acetone	R-Cu-1-A	1.882	11.56	127
		1.394	12.97	127
		1.212	20.87	127
		0.757	20.87	127
		0.635	20.87	127
Acetone	R-Cu-4-6	1.5268	7.15	121
		1.0267	9.80	121
Acetone	R-Cu-Ni-2	1.9568	11.97	98.5
		1.0584	12.82	98.5
Acetone	R-Cu-Ni-3	2.1700	13.14	98.5
		0.8897	13.98	98.5
Acetone	R-Cu-Ni-4	1.3251	20.33	98.5
		1.1104	22.03	98.5
Mesityl oxide	R-Cu-4-9	0.8871	55.38	127
		0.5233	55.38	127
		0.1641	55.38	127

too much catalyst weight. In a study of hydrogenations of d-limonene with Raney nickel, they found that the weight of catalyst had to be below 0.3 g. for consistent results.

Influence of Added Metals on the Rate of Copper Catalysts.--In order to study the effect of added metals on a Raney type copper catalyst, different proportions of nickel, cadmium, and zinc were used in preparing the alloys.

The percentage by weight of the catalysts along with the rates of reaction of the various catalysts is given in Table 16.

An induction furnace was used to achieve the high temperature necessary to melt the nickel in those alloys which contain it. R-Cu-Ni-1 was not mixed properly on preparation, since the nickel solidified as the copper and aluminum were added. The catalyst prepared from this alloy has a very low activity. The other alloys were all mixed thoroughly and all the catalysts were prepared identically.

The interpolated rates for R-Cu-4-4, R-Cu-3 and Raney nickel are also given in Table 16. The percentage of aluminum in R-Cu-4-4 was different from the others and the method of preparation of Raney nickel and R-Cu-3 differed from all the others. It is probably better to use R-Cu-4-4 for comparison, since there was less difference between the rates of R-Cu-3 (50 per cent Cu, 50 per cent Al; k/g. = 21.63) and R-Cu-4 (40 per cent Cu, 60 per cent Al; k/g. = 25.12), where the method of preparation was the same, than between the rates of

Table 16. Effect of Added Metals on the Rate of Hydrogenation of Acetone.

Catalyst	%Cu	%Al	%Ni	%Cd	%Zn	Rate Constant ($k \times 10^4$) ($min.^{-1}\ g.^{-1}$)	Temperature (^{o} C.)
R-Cu-Ni-1	10	50	40			1.21	100.0
R-Cu-Ni-2	25	50	25			12.39	98.5
R-Cu-Ni-3	40	50	10			13.56	98.5
R-Cu-Ni-4	10	50	40			21.18	98.5
R-Cu-4-4	40	60				26.55	98.5
R-Cu-3	50	50				8.07	98.5
R-Ni						75.33	98.0
R-Cu-Cd-1	10	50		40		1.11	128.0
R-Cu-Cd-4	39.4	60		0.6		23.55	128.0
R-Cu-4-4	40	60				65.16	128.0
R-Cu-Zn-1	45	35			20	1.50	96.5
R-Cu-Zn-2	45	20			35	0.00	169.0
R-Cu-Zn-3	45	50			5	13.67	94.5
R-Cu-4-4	40	60				23.28	94.5

R-Cu-4 and R-Cu-4-4 (k/g. = 60.95), where the method of preparation differed.

The activity of the catalyst, then, drops as copper is added to pure nickel up to the 50 per cent mixture, after which the rate increases again until 100 per cent copper is reached.

According to Reynolds[25], no Raney copper catalyst is very active for the hydrogenation of benzene. His curve of composition versus rate falls from pure nickel to a low point at 50 per cent copper, after which more copper has little effect. The fact that copper is not suitable for the hydrogenation of benzene may explain the difference between Reynolds' results and the results given here.

The copper-cadmium alloys that were prepared gave catalysts which were made up of separate particles of copper and cadmium, since the solubility of cadmium in copper[26] is 2.8-3.0 per cent at 555° C., the temperature at which the cadmium was added to the copper-aluminum melt. The solubility of copper in cadmium is low also, being 0.05-0.1 per cent[27] at 270° C. Aluminum is insoluble in cadmium, and cadmium dissolves in aluminum to an extent of only about 0.97 per cent at 550° C.[28]

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[25]P. W. Reynolds, J. Chem. Soc., 1950, 265.

[26]S. A. Pogodin, V. I. Mikheeva, and G. A. Kagan, Ann. inst. anal. phys. Chim. (U.S.S.R.) 7, 34 (1935).

[27]G. Tammann and A. Heinzel, Z. anorg. allgem. Chem., 176, 147 (1928).

[28]M. Hansen and B. Blumenthal, Metallwirtshaft, 10, 925 (1931).

One run was made with one of the non-homogeneous catalysts (R-Cu-Cd-1). The catalyst sample was taken from the bottle of catalyst after agitating it in order to mix the particles thoroughly. If the cadmium exerted no poisoning effect on the copper, it would have reduced the rate with this alloy by about 75 per cent, since the weight of catalyst was about 75 per cent cadmium. Table 16 shows that the rate for R-Cu-4-4 is about 59 times that of R-Cu-Cd-1.

R-Cu-Cd-4 was prepared to assure a heterogeneous alloy by using less than one per cent cadmium. Only 0.6 per cent cadmium was found to decrease the rate markedly, although it did not completely inactivate the catalyst.

Corson and Ipatieff[29] found the same thing to be true in the hydrogenation of benzene. They state that 0.1 to 0.2 per cent cadmium inactivated a reduced carbonate copper-nickel catalyst almost completely.

A study of the effect of an added metal replacing aluminum was made. Added zinc effects the rate because it is less easily dissolved by sodium hydroxide than is aluminum. It was found that as the zinc content increases, the rate of hydrogenation decreases, as is expected.

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[29] B. B. Corson and V. N. Ipatieff, J. Phys. Chem., 45, 431 (1941).

CHAPTER VI

TOPICS FOR FURTHER STUDY

Poisoning of Raney Copper.--This investigation has shown that the aging of Raney copper catalysts causes a linear drop in the experimental rate constant. It appears that the activity of Raney copper does not decrease as quickly as does Raney nickel. The question presents itself, then, as to how easily the copper catalyst is poisoned. Raney nickel is poisoned readily by many materials, amongst which are compounds containing sulfur or chlorine.

It would be interesting to learn if copper is less sensitive to poisoning than nickel, as it is in the aging process. Such a study could be carried out by introducing a fixed amount of sulfur or chlorine-containing material into the reaction liners and comparing the percentage drop in rate with both Raney nickel and Raney copper catalysts.

Rate Studies of Other Compounds.--A further study of the rates of hydrogenation of different compounds would be of value also. Such a study would involve the determination of rates of hydrogenation of several straight chain compounds containing carbonyl groups, unsaturation, et cetera; as well as the branch chain isomers. This would determine the effect of position of the reducible group as well as the effect of branching of the molecule.

Van Mechelen and Jungers make the claim that the reduction of the carbonyl group in any of the simple aliphatic compounds they studied has the same activation energy. This investigation would include such a study of the activation energies of both carbonyl compounds and others.

The double bond in mesityl oxide hydrogenated preferentially because the double bond is conjugated with a carbonyl group. Information on the initial products of hydrogenation of a compound where two or more reducible groups are present, but not in conjugation with each other, would be of interest. It has already been stated that the carbonyl group when present alone in a compound is more quickly hydrogenated than a double bond or a nitro group is under similar circumstances.

Effect of Added Metals.--Another topic of considerable interest is the effect of other metals on the activity of catalysts. Ipatieff and co-workers have stated that the addition of a very small percentage of nickel to a reduced copper catalyst decidedly increases the rate of hydrogenation. Investigation of many different catalysts prepared from varying amounts of nickel and copper with a standard percentage of aluminum throughout would show if there are any irregularities such as Ipatieff described with Raney copper. Calculation of the surface area as well as the rate constants of various catalysts, such as that done by Reynolds with benzene, would be profitable with acetone, since acetone is more easily reduced by

copper and changes in rates, therefore, would be magnified.

Finally, other metals, such as iron and cobalt, could be incorporated in a copper catalyst to determine their effect.

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V I T A

VITA

Paul Edward Robbins was born April 4, 1928 in Camden, New Jersey. He is the son of Olga (nee Dorn) and Charles H. Robbins. His elementary school education was received at the Toms River, Audubon, and Erlton schools in New Jersey. He attended the Haddonfield Memorial High School and graduated in June 1945. After working one year for the R. M. Hollingshead Company, in Camden, New Jersey, he enlisted in the Army of the United States. He worked in the Schofield Barracks' Post Office until his discharge in August, 1947. After working one more year at R. M. Hollingshead Company, he began his college education at the University of Pennsylvania in Philadelphia. During the summers he worked in the laboratories of Campbell Soup Company. He graduated in June, 1952 with the degree of Bachelor of Science in Chemistry. In September, 1952 he came to the Georgia Institute of Technology for graduate work. He held a teaching assistantship for a year, after which he received a fellowship from the Office of Ordnance Research. While at Georgia Tech he married Gladys Evelyn Cordray of Savannah, Georgia.